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Shell NO_x/SO_2 Flue Gas Treatment Process: Independent Evaluation

by

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ABSTRACT

Nitrogen oxide emissions from stationary sources may be reduced by 80 to 90 percent through the application of selective catalytic reduction (SCR) of NO_x with ammonia. In the interest of furthering the development of this technology, EPA sponsored pilot scale tests of two SCR processes treating flue gas slip streams from coal-fired boilers. One of the processes tested was the Shell Flue Gas Treating (SFGT) process which also removes SO_2. The results of an independent evaluation of the SFGT pilot plant tests show that the process is capable of simultaneously reducing NO_x and SO_2 emissions by 90 percent even though this was not demonstrated during the pilot plant test program. The process design tested appeared well suited to coal-fired application and the reactor processed flue gas for 2000 hours without any signs of plugging. Results of an energy analysis indicates the SFGT process energy requirements equal 5 percent of the boiler's capacity. Process costs were estimated based on the pilot plant test results. Estimated capital investment and annual revenue requirements for the SFGT process are $168/kW and 9.60 mills/KWh respectively. These costs are significantly higher than previous estimates for the process using the same process design.

SECTION 1

SUMMARY

1.1 INTRODUCTION

Selective catalytic reduction (SCR) of NO_x with NH_3 is capable of reducing NO_x emissions by 80 percent or more. As such, SCR represents the most effective process available for controlling stationary source NO_x emissions. For a utility application of SCR, a catalytic reactor is located between the economizer and air preheater sections of the boiler. At this location the flue gas temperature ranges from 300 to 400°C (570-750°F) which is optimum for the catalytic activity. Ammonia is injected into the flue gas upstream of the catalyst and reacts with NO_x on the catalyst surface to form elemental nitrogen and water.

Most SCR processes were developed and are being operated commercially in Japan, primarily on gas- and oil-fired sources. However, in the U.S., SCR systems are now being installed on a limited basis. The most notable application is a demonstration system that is being constructed to treat one-half of the flue gas from Southern California Edison's 215 MWe Huntington Beach Unit No. 2 (an oil-fired boiler). The operation of this system is expected to establish SCR as a commercially available technology for oil- and gas-fired sources in the U.S.

In Japan, development efforts are currently aimed at applying SCR to coal-fired sources. To date, most of the SCR process vendors in Japan have operated pilot units on slip-streams from coal-fired boilers. In addition, there are now four full-scale SCR systems treating flue gas from coal-fired boilers with another eight units scheduled for start-up in 1982 and 1983. These development efforts are rapidly establishing SCR as commercially available technology for controlling NO_x emissions from coal-fired sources in Japan.

The transfer of SCR technology from Japan to the U.S. for coal-fired applications presents a potentially significant problem. Since most coal-fired boilers in the U.S. operate ESP's located downstream of the air preheater, a typical SCR application would expose the catalyst in the reactor to the full particulate concentration from the boiler. Although tests have been conducted in Japan in which the catalyst was exposed to high particulate concentrations with no adverse effects, the differences in the composition of particulates from U.S. and Japanese coals could impact SCR operation.

In an effort to further the development of SCR technology and to determine how differences between Japanese and U.S. coal/particulate properties impact the performance of SCR processes, EPA has sponsored pilot scale (0.5 MW equivalent) tests of two SCR systems. The SCR systems tested were the Hitachi Zosen (HZ) process and the Shell Flue Gas Treating (SFGT) process, which is also capable of removing SO_2 from the flue gas. In both cases, the pilot plants processed a flue gas slipstream from a coal-fired boiler. The contractors responsible for the design and operation of these pilot plants were Chemico Air Pollution Control Corporation, which is the North American licensee for the HZ process, and the Process Division of UOP, who is the licensing agent of the SFGT process. These contractors were also responsible for collection, evaluation, and reporting of the test data.

The primary objectives of the pilot plant test programs sponsored by EPA were: (1) to demonstrate the ability of the processes to achieve a 90 percent reduction in NO_x emissions, and in the case of the SFGT process, a simultaneous 90 percent reduction in SO_2 emissions, and (2) to determine the impacts of catalyst performance which result from processing flue gas from a coal-fired utility boiler.

In conjunction with the pilot plant test program, EPA contracted Radian Corporation to prepare an independent evaluation of the processes tested based on the pilot plant results. This section summarizes the results of the independent evaluation of the SFGT process. It includes a discussion of the results of tests conducted by both UOP and Radian and the results of Radian's independent evaluation of the SFGT process. A separate report covering the detailed results of the pilot plant test program has been prepared by UOP.

1.2 PROGRAM OBJECTIVES AND APPROACH

The independent evaluation of the SFGT pilot plant test program conducted by Radian Corporation had three major objectives. The first was to provide independent validation of the process measurements made by UOP. The second objective was to quantify any changes in the emission rates of secondary pollutants across the pilot plant reactor. And the third objective was to complete a technical and economic evaluation of the SFGT process including identification of areas which require further development or investigation.

In order to validate the measurements made by UOP, a quality assurance program was implemented. This program used EPA reference methods and other standard measurement techniques to make independent audits of critical process parameters such as flue gas flowrate, NH_3 injection rate, etc. In conjunction with the quality assurance program, the continuous NO_x and SO_2 monitors were subjected to certification tests designed to determine the monitors' ability to make accurate, repeatable measurements. These certification tests included measurement of the continuous monitors relative accuracy, drift, calibration error, and response time.

Concurrent with the quality assurance program, a stack sampling program was conducted to measure changes in secondary process emissions across the SCR reactor. This approach required simultaneous sampling of the reactor inlet and outlet for the species of interest. The samples were then analyzed and differences between inlet and outlet concentrations determined.

Based on the results of the quality assurance program, the stack sampling program, and the test data collected by UOP, an evaluation of the SFGT process was completed by Radian. This evaluation consisted of several steps. First, the test data were analyzed and reduced to a form which could be used to predict process performance for a specified set of operating conditions. Then, using the reduced test data and the results of the stack sampling program, material and energy balance calculations were completed for a 500 MWe coal-fired application of the SFGT process. The basis for these calculations was identical to that used by TVA in developing cost estimates for the SFGT process and presented in "Preliminary Economic Analysis of NO_x The Gas Treatment Processes".[1] The results of the material and energy balance calculations were then used to develop a modified estimate of total capital investment and annual revenue requirements for a 500 MW coal-fired application of the SFGT process. Finally, the test data were reviewed and areas requiring further investigation/quantification were identified.

1.3 RESULTS

Several areas which influence the technical and economic feasibility of the SFGT process were examined as part of this study including:

- the pilot plant test results,
- the results of Radian's independent tests,
- the results of a 500 MW conceptual design of the SFGT process,
- the material balance calculations for a 500 MW SFGT process application,
- the energy balance calculations for a 500 MW SFGT process application, and
- the estimated capital investment and annual revenue requirements for a 500 MW SFGT process application.

The following discussion summarizes the results of the evaluation of each of these areas while Section 1.4 presents overall conclusions on the technical and economic feasibility of applying the SFGT process to a coal-fired boiler.

1.3.1 Pilot Plant Test Results

The test program at the SFGT pilot plant was initiated in October 1979, and was completed in October 1980. During this period, the pilot plant processed a flue gas slip stream from between the economizer and the air preheater of the coal-fired unit No. 2 at Tampa Electric Company's Big Bend Station. Normal flue gas flowrate to the pilot unit was 1600 Nm^3/hr (1000 scfm) and flue gas was processed for a total of about 2000 hours during the program.

The pilot plant test program involved examination of three charges of acceptor* material under a variety of test conditions, including tests for simultaneous reduction of NO_x and SO_2 emissions and tests for removal of only NO_x or SO_2. In general, these tests were divided into two categories: optimization tests and demonstration or long-term tests. The objective of the optimization tests was to identify operating conditions which would reduce both NO_x and SO_2 emissions by 90 percent at a minimum total cost for operating the process. The major objective of the demonstration tests was to document the ability of the process to achieve a 90 percent reduction in NO_x and SO_2 emissions for 90 days.

The objectives of the pilot plant tests conducted by UOP were not met. Under typical operating conditions, SO_2 removal was 90 percent while the NO_x reduction efficiency averaged only about 70 percent. This was due to poorer than expected performance of the acceptor. As a result, the pilot plant reactor was undersized for the flue gas composition at the Tampa Electric site. While the overall program objectives were not met, the tests did document the technical feasibility of applying the SFGT process to a coal-fired power plant.

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*"acceptor" is the term for the material which both catalyzes the NO_x reduction reactions and removes SO_2 from the flue gas.

The pilot plant operated for approximately 2000 hours with no signs of plugging in the reactor and no soot blowing as required.

In terms of process performance, the pilot plant tests did not demonstrate simultaneous reduction in NO_x and SO_2 emissions at design operating conditions. However 90 percent NO_x/SO_2 reduction was achieved through the use of a pre-oxidation and cooling step which was not included in the original process design. Extrapolation of the pilot plant test results indicate that it should be possible for the process to reduce NO_x and SO_2 emissions by 90 percent without preoxidation and cooling. However, this requires a larger reactor and the use of additional acceptor which will significantly impact the estimated costs for the SFGT process. Because of this cost impact and the good performance achieved through the use of preoxidation and cooling steps, UOP now proposes to include these steps in the commercial design and operation of the SFGT process.

The test program briefly examined the effects of key operating parameters but did not provide a detailed characterization of the effects of various operating parameters on process performance. Two parameters in particular, temperature and flowrate, were shown to affect process performance, yet their effects were not thoroughly documented. Temperature and flowrate are significant parameters since they would be expected to change with swings in boiler load, thus changing NO_x and SO_2 emission reduction efficiencies.

Probably the most important aspect of the SFGT process performance which was documented during the pilot plant tests was the stability of acceptor activity. The test results showed that upon first exposure to flue gas, the acceptor experienced an initial decline in activity, but then remained stable over the course of 700 hours of operation. This is favorable in terms of applying the process to a coal-fired boiler since, after the initial decline, there was no measurable change in activity. However, it should be noted that this doe not document acceptor activity over a period of time equivalent to one year of commercial operation. While demonstration of a one year acceptor life was not an objective of the test program, a one year acceptor life is critical to the economic feasibility of the SFGT process. And, if the acceptor can maintain activity for longer than a year, this could result in a significant reduction in process costs.

Overall, the pilot plant test results indicate that application of the SFGT process to a coal-fired boiler is technically feasible. However, these tests did not demonstrate several key factors, including:

- the ability of the process to simultaneously reduce NO_x and SO_2 emissions by 90 percent under design operating conditions,
- the performance of the process under conditions which simulate reduced boiler loads, and
- the stability of the acceptor over a period equivalent to 1 year of commercial operation.

Of these factors, the one most critical to the commercial success of the process is the stability of the acceptor. Althrough this was not demonstrated it should be noted that no deterioration of acceptor performance was observed during the program and that UOP should guarantee a one year acceptor life for a commerical application of the process.

1.3.2 Independent Evaluation Test Program Results

The independent evaluation test program conducted by Radian had two primary objectives: to insure the quality of the data collected at the SFGT pilot plant and to quantify changes in the concentrations of certain pollutants across the SFGT reactor. Data quality was determined by quality assurance (QA) audits and continuous monitor certification tests, while changes in pollutant concentrations were determined by a secondary emissions sampling program. The results of each of these elements of the independent evaluation program are summarized below.

Quality Assurance Audits

The QA audits conducted by Radian were designed to insure that the process data which are required to characterize the operation of the SFGT pilot plant were accurate. Radian employed reference methods for auditing process operating parameters which were measured on a continuous or routine bases by UOP. One exception to this was the measurement of NH_3 emissions which were not routinely monitored by UOP, although the original design of the pilot unit included an analyzer intended to determine NH_3 emissions.

The results of the NH_3 emissions sampling are presented in Table 1-1. Samples were collected during both NO_x/SO_2 tests and NO_x-only tests. As shown, the samples taken during the NO_x-only tests indicate relatively high NH_3 emissions which averaged 49 ppm. But the samples collected during NO_x/SO_2 tests indicated NH_3 emissions averaged about 15 ppm. At the 15 ppm level, NH_3 emissions are not expected to result in any significant operational or environmental problems. However, these emissions are not expected to be representative of a commercial SFGT process designed for 90 percent reduction of NO_x and SO_2. Changes in reactor design required to achieve the 90 percent NO_x/SO_2 reduction can result in a significant increase in the NH_3 emissions.

TABLE 1-1. SFGT PILOT PLANT NH_3 EMISSIONS

Mode of Operation	NO_x In (ppm dry)	$NH_3:NO_x$	NH_3 Emissions (ppm dry)
NO_x/SO_2	380	1.17	15
NO_x/SO_2	420	1.21	16
NO_x/SO_2	390	1.31	22
NO_x/SO_2	375	1.25	17
NO_x/SO_2	-	-	16
NO_x/SO_2	-	-	11
NO_x/SO_2	392	1.17	12
NO_x/SO_2	402	1.19	13
NO_x/SO_2	-	-	16
NO_x Only	420	1.18	47
NO_x Only	327	1.21	52
NO_x Only	224	1.38	48

The results of the other QA audits conducted by Radian are summarized in Table 1-2. As shown, all but the flue gas flowrate measurements were within 10 percent of the values recorded by UOP. In general, the QA audit results indicate that the process data collected by UOP accurately characterize the operation of the SFGT pilot plant. However, the discrepancy in the flowrate measurements indicated there could be a problem with this measurement technique and the reactor may have been processing flue gas at greater than design flowrates. This question was resolved during subsequent tests in which UOP confirmed the accuracy of their flowrate measurement by an independent test.

TABLE 1-2. QA AUDIT RESULTS

Measurement Audited	Audit Procedure	Relative[1] Error (%)
Flue Gas Flowrate	EPA Reference Method 2	-14.4
NH_3 Injection Rate	Absorption followed by wt gain measurement - (analogous to EPA Method 4)	7.6
Reactor Pressure Drop	Magnehelic differential pressure gauge	-1.4
Reactor operating temp.	Thermocouple with traverse of reactor inlet	-1.3

[1] Relative error = $\frac{(\text{Process measurement - Audit result})}{(\text{Audit result})} \times 100\%$

Based on the results of the QA audits and subsequent tests by UOP, the major process measurements made by UOP were determined to be accurate within the limits of the techniques employed to make the measurements. This indicates that the data collected by UOP can be used to characterize operation of the process.

Secondary Emissions Sampling

The secondary emissions sampling program was conducted by Radian during June and July 1980, concurrent with demonstration tests conducted by UOP. The objective was to quantify changes in the emission rates of pollutants other than NO_x and SO_2. For the most part, these tests were conducted during tests in which both NO_x and SO_2 were being removed from the flue gas.

Table 1-3 summarizes the results of the secondary emissions sampling program at the SFGT pilot plant. As shown, concentrations of both hydrogen cyanide (HCN) and nitrosoamines at the reactor outlet were below the detection limit of the analytical techniques employed. For HCN, this detection limit is equivalent to 10 ppbv and for N-Nitrosodimethylamine, 2 ppbv. In both cases, these concentrations are below the level which is considered safe for emission sources.

Decreases in both the hydrocarbon and carbon monoxide concentrations were measured across the reactor. This change is probably due to oxidation of these pollutants in the reactor. Table 1-3 also shows that a decrease in SO_3 concentration was also measured across the reactor. This decrease is due to removal of SO_3 from the flue gas in the SFGT reactor. The apparent change in particulate concentration shown in the table is believed to be due to unaccounted for stratification in the ducts. It should be noted that no results for nitrous oxide (N_2O) are presented. This is due to the fact that the analytical technique used to measure N_2O proved unsatisfactory for use in a flue gas stream.

TABLE 1-3. STACK SAMPLING RESULTS AT THE SFGT PILOT PLANT

Flue Gas Component	Reactor Inlet Concentration[1]	Reactor Outlet Concentration[1]	Measurement Technique
Nitrosoamines[2]	<5 µg/dscm[3]	<5 µg/dscm	Absorption, extraction, gas chromatograph w/nitrogen specific detector
Hydrogen Cyanide	<.01 mg/dscm	<.01 mg/dscm	Absorption, distillation, titration
Sulfur Trioxide	11.4 ppmv (dry basis)	0.1 ppmv (dry basis)	Controlled condensation, ion chromatograph
Hydrocarbons (C_1-C_6)	28.5 ppmv	21.0 ppmv	Gas chromatograph flame ionization detector
Carbon Monoxide	0.13%	<0.017%[2]	Fischer gas partitioner
Nitrous Oxide	-	-	Infrared spectroscopy
Particulates	8.9 gm/dscm	6.3	In stack filter

[1] Average of 2 or more tests.
[2] Below the detection limit.
[3] dscm = dry standard cubmic meters.

In addition to measuring the concentration of particulates in the flue gas, an elemental analysis of the particulates was completed in an attempt to determine if erosion of the acceptor has a measurable effect on particulate composition. Table 1-4 presents the results of the elemental analysis of the particulates collected at the SFGT pilot plant. As shown, no significant change in the composition of the particulates was measured with respect to these elements. The changes which are shown in Table 1-4 are due to random errors in the sampling or analysis technique and are not representative of real changes in particulate composition.

TABLE 1-4. RESULTS OF PARTICULATE ANALYSIS AT THE SFGT PILOT PLANT[1]

Component	In	Out	Out/In
Al	8.6%	8.0%	.93
Ca	1.8%	1.8%	1.00
Fe	12%	11.1%	0.93
K	1.5%	1.4%	0.93
Mg	5100 ppm	5000 ppm	0.98
Mn	300 ppm	320 ppm	1.07
Sn	270 ppm	270 ppm	1.00
Na	4300 ppm	5100 ppm	1.19
Si	20%	16%	0.80
Zn	410 ppm	720 ppm	1.76
Cu	96 ppm	100 ppm	1.04
Ti	5400 ppm	5100 ppm	0.94
V	255 ppm	340 ppm	1.33

[1] Concentrations are on a mass fraction basis.

Of the secondary emissions sampling results, the most significant was the fact that SO_3 is removed in the SFGT reactor. The removal of SO_3 in the reactor results in a reduction of the sulfuric acid dewpoint which permits additional heat recovery in an air preheater located downstream of the SFGT process. The additional heat recovery tends to reduce the energy requirements of the process and consequently reduces process costs.

Continuous Monitor Certification Tests

Certification tests were conducted for the SO_2 and NO_x monitors used to measure flue gas concentrations of pollutants at the inlet and outlet of the reactor. Thee tests were included in the independent evaluation program to insure the quality of the pilot plant performance data being collected by UOP. Certification of continuous emission monitors involves a formal procedure which has been developed by EPA to insure the accuracy of monitors measuring emisions from sources which must comply with new source performance standard emission limitations. In order for a continuous emission monitor (CEM) to be certified, it must be subjected to and pass a number of performance tests, including:

- calibration error,
- response time,
- drift, and
- relative accuracy.

The performance specifications for each of the above certification tests are presented in Table 1-5 along with the results of the certification tests. The performance specifications are those contained in the Federal Register, Vol. 44, No. 197, Wednesday, October 10, 1979 - "Proposed Rules: Standards of Performance for New Stationary Sources; Continuous Monitoring Performance Specifications".

As shown in Table 1-5, the test results for both the NO_x and SO_2 continuous monitors met the performance specifications with one exception; the relative accuracy of the outlet NO_x monitor was over 50 percent, while the performance specifications require a relative accuracy of 20 percent or less. These data indicate that with the exception of the outlet NO_x analyzer, the continuous monitors were making accurate measurements of flue gas NO_x and SO_2 concentrations.

TABLE 1-5. RESULTS OF THE CONTINUOUS MONITOR CERTIFICATION TESTS AT THE SFGT PILOT PLANT

Certification Test	Performance Specification	Inlet SO_2[1] Monitor	Outlet SO_2[1] Monitor	Inlet NO_x Monitor	Outlet NO_x Monitor
Calibration Error					
-high level (%)	≤ 5	1.4	1.4	3.85	2.52
-mid level (%)	≤ 5	0.7	0.7	4.62	2.62
Response Time (min)	≤ 15	0.8	1.3	1.7	0.8
Zero Drift (%) (2-hour)	≤ 2	0.25	0.25	0.64	1.04
Calibration Drift (%) (2-Hour)	≤ 2	0.49	0.49	1.35	1.18
Relative Accuracy (%)	≤ 20 [2]	14.0	8.6	12.6	52.3

[1] One instrument was used to measure both inlet and outlet of the reactor.
[2] Alternatively, ≤ 10 percent of the applicable emissions standard.

The poor relative accuracy of the outlet NO_x analyzer shown in Table 1-5 would tend to indicate that the monitor was making inaccurate measurements of flue gas NO_x concentrations. However, there are several factors which must be considered when evaluating these test results. First, the absolute error in the Method 7 versus the monitor measurements was only 16 ppm on the average. This is a relatively small difference. A second factor, which indicates that the outlet NO_x monitors performance was within acceptable limits, is that the performance specifications require the relative accuracy be less than or equal to 20 percent or 10 percent of the applicable standard, whichever is greater. Using the NSPS for bituminous coal-fired sources as a basis, the relative accuracy of the outlet NO_x monitor is approximately 5 percent of the standard which is within acceptable limits.

Overall, the results of the certification tests indicate that the continuous NO_x and SO_2 monitors at the SFGT pilot unit were performing acceptably. Therefore, the data collected during the pilot plant tests by UOP is representative of the pilot plant's performance. This is partially a result of UOP's extensive monitor maintenance program which was designed to insure the accuracy and quality of the performance data collected.

1.3.3 Results of the Conceptual Design of a 500 MW SFGT Process

A conceptual design of a 500 MW SFGT process was prepared based on selected pilot plant test results. This conceptual design served as a basis for material and energy balance calculations and for a cost estimate for a 500 MW application of the SFGT process.

Table 1-6 summarizes the results of the conceptual design for a 500 MW application of an SFGT process. As shown, the key design variable levels are presented. The results of this design indicate that it is technically possible to simultaneously reduce NO_x and SO_2 emissions by 90 percent using the SFGT process without the use of preoxidation and cooling steps. However, the reactor size and the quantity of acceptor required to meet the design NO_x and SO_2 reduction efficiencies are significantly greater than previous estimates (based on the same type of process operation) indicated.

TABLE 1-6. RESULTS OF THE SFGT CONCEPTUAL DESIGN

Parameter	Design Level Developed in this Study
Acceptance Time (min)	148
Reactor Depth (meters)	9
Inlet SO_2 Concentration (ppm)	2548
Recycle Rate (%)	1.8
NH_3/NO_x Injection Ratio	1.5
Overall NO_x/SO_2 Reduction (%)	90
NO_x/SO_2 Reduction Across Reactor (%)	89.8
Number of Reactors	8
Crossectional Area Of Each Reactor (m^2)	40.75
SFGT System Pressure Drop (kPa)	3.93

To some extent, the increase in the quantity of acceptor is a function of the limitations placed on the conceptual design to reflect pilot plant operation. Data were collected which indicate substantial improvement in NO_x and SO_2 reduction efficiencies could be achieved through modification of process operation. But, limitations of the pilot plant prevented adequate characterization of process performance under modified operating conditions.

Reactor pressure drop and other design parameters are fairly consistent with previous estimates for the processes. The results do, however, indicate the need for equipment to control the temperature and flowrate of the flue gas entering the reactor. This is primarily due to the fact that the SO_2 reaction rate is reduced at reduced temperatures and flowrates and data were not developed to characterize overall process performance under conditions which simulated reduced boiler loads.

In summary, the conceptual design indicates that the SFGT process can simultaneously reduce NO_x and SO_2 emissions by 90 percent. However, this level of emissions reduction is achieved only at the expense of an increased quantity of acceptor and a corresponding increase in costs. It should be noted that there may be other means of improving process performance, but these were not considered in preparing the conceptual design.

1.3.4 Results of the Material Balance Calculations for a 500 MW SFGT Process

Material balance calculations for a 500 MW application of the SFGT process were included as part of this study to identify raw material requirements for the process and to serve as a basis for an estimate of capital investment and annual revenue requirements. The material balance was based on the pilot plant and secondary emissions sampling test results and thus reflects those results in the estimated process and component flows. The most significant results of the material balance calculations include estimation of hydrogen, steam, and NH_3 requirements and NH_3 and SO_3 emissions from the process.

Table 1-7 summarizes some significant results of the material balance calculations and compares those results with the material requirements identified by TVA in their preliminary economic analysis. As shown, hydrogen requirements increase by approximately 25 percent. This is due to the fact that H_2 consumption in the pilot plant was higher than previous estimates indicated. Steam requirements increased by the same fraction which indicates that the steam to H_2 ratio used in the TVA design is essentially identical to the ratio used during the pilot plant tests. The naphtha requirements increase in direct proportion to the hydrogen requirements. This is perhaps the single most important increase in a material flowrate since it has a significant impact on annual revenue requirements for the process. The NH_3 requirements increase significantly due to the high NH_3/NO_x ratio used in preparing the conceptual design. This reflects the relatively poor performance of the pilot plant at lower NH_3/NO_x injection ratios. Finally, the quantity of sulfuric acid is essentially unchanged since the same quantity of SO_2 is being removed from the flue gas.

TABLE 1-7. A COMPARISON OF MATERIAL FLOWS FOR A 500 MW COAL-FIRED APPLICATION OF THE SFGT PROCESS

Material Requirement	Estimated Flowrate TVA[1]	 Radian[2]	Ratio
Steam (kg/hr)	31,940	40,300	1.26
Hydrogen (kg/hr)	1,300	1,630	1.25
Naphtha (m^3/hr)	57	71	1.25
NH_3 (kg/hr)	830	1,120	1.35
H_2SO_4 from acid plant (kg/hr)	16,160	16,160	1.00

[1] Estimated prior to pilot plant test program.
[2] Based on pilot plant test results.

1.3.5 Results of the Energy Balance Calculations for a 500 MW SFGT Process

An energy balance was completed as part of the evaluation of the SFGT process. This energy balance defined overall process energy requirements and quantified the heat credits associated with the process. The results of the analysis of energy requirements indicated that the SFGT process has a net energy consumption equivalent to 5 percent of the energy input to the boiler.

The individual components of the overall process energy requirements are summarized in Table 1-8. As shown, the single largest component of the overall energy requirement is the fuel energy which could be obtained through combustion of the naphtha used to generate hydrogen. This represents over 5 percent of the equivalent energy consumed by the boiler and it is directly dependent on the H_2 requirements of the process. Because the fuel energy requirement is so large, a given percentage decrease in H_2 requirements would result in approximately an equivalent percentage decrease in overall energy requirements for the process. This is a strong basis for further examination of H_2 requirements and the factors which affect H_2 consumption.

TABLE 1-8. OVERALL ENERGY REQUIREMENT FOR A 500 MW APPLICATION OF THE SFGT PROCESS

Energy Area	Energy Requirement (Gcal/hr)	Percent of Boiler Capacity
Heat Credit	(35.75)	(3.2)
Steam	6.98	0.6
Electricity	22.3	2.0
Fuel	63.0	5.6
TOTAL	56.53	5.0

The energy requirements associated with steam and electrical energy are less than 50 percent of the fuel energy requirements. In the case of steam, this represents a small fraction of the overall energy requirements of the process and although some reduction in steam consumption may be possible, it will not significantly influence the annual revenue requirements. In the case of electrical energy, the major portion of this requirement results from the energy of fan compression. This can be reduced by reducing acceptor volume.

The heat credits associated with the SFGT process were estimated to be equivalent to over 3 percent of the energy input to the boiler and result in nearly a 40 percent decline in the overall energy requirements for the process. The heat credit analysis indicated that nearly all of the potential heat credits can be recovered in a commercial application of the SFGT process.

1.3.6 Results of the Cost Estimate for a 500 MW SFGT Process Application

An estimate of total capital investment and annual revenue requirements for a 500 MW application of the SFGT process was prepared as part of this evaluation. The estimated costs reflect the results of the pilot plant tests. When compared with the previous estimate prepared by TVA, the modified cost estimates indicate the magnitude of the impact the pilot plant results had on estimated process costs. In addition, comparison of the modified cost estimate with cost estimates for other SCR processes is an indicator of the cost effectiveness of the SFGT process as tested in the pilot plant program.

Results of Capital Cost Estimate

Table 1-9 presents the individual components and the estimated total capital investment for a 500 MW application of the SFGT process. As shown, the total capital investment was estimated to be approximately $\$84.2 \times 10^6$ which is equivalent to \$168/kW of generating capacity. When compared to TVA's previous estimate of $\$67.2 \times 10^6$ this represents about a 25 percent increase in total capital investment. The principal difference between the two estimates is the estimated acceptor volume. The required acceptor volume based on the pilot plant tests was estimated to be nearly 90 percent greater, thereby increasing the total capital investment.

Results of the Annual Revenue Requirement Estimate

Table 1-10 presents the individual components and the total estimated average annual revenue requirements for a 500 MW application of the SFGT

TABLE 1-9. ESTIMATED CAPITAL INVESTMENT FOR A 500 MW APPLICATION OF THE SFGT PROCESS[a]

	Investment, $	% of total direct investment
Direct Investment[b]		
NH_3 storage and injection	890,000	1.9
H_2SO_4 plant	7,172,000	15.2
Reactor section	27,455,000	58.1
Flow smoothing section	2,828,000	6.0
Steam Naphtha reformer	4,698,000	9.9
Gas handling	1,546,000	3.3
Sub-total direct investment (DI)	44,589,000	94.4
Services, utilities (0.06 x DI)	2,675,000	5.6
Total direct investment (TDI)	47,264,000	100.0
Indirect Investment		
Engineering design and supervision	709,000	1.5
Architect and engineering contractor	177,000	0.4
Construction expense = 0.25 $(TDI \times 10^{-6})^{0.83}$	6,135,000	13.0
Contractor fees = 0.096 $(TDI \times 10^{-6})^{0.76}$	1,799,000	3.8
Total indirect investment (IDI)	8,820,000	18.7
Contingency = 0.2 (TDI + IDI)	11,217,000	23.7
Total fixed investment (TFI)	67,301,000	142.4
Other Capital Charges		
Allowance for startup and modifications = (0.1) (TFI)	6,730,000	14.2
Interest during construction = (0.12) (TFI)	8,076,000	17.1
Total depreciable investment	82,107,000	173.7
Land	14,000	-
Working Capital	2,051,000	4.4
TOTAL CAPITAL INVESTMENT	84,172,000	178.1

[a] Basis: 500 MW new coal-fired power plant, 3.5% sulfur coal, 90% NO_x removal, 90% SO_2 removal. Midwest plant location. Represents project beginning mid-1977, ending mid-1980. Average basis for scaling, mid-1979. Investment requirements for fly ash disposal excluded. Construction labor shortages with overtime pay incentive not considered.

[b] Each item of direct investment induces total equipment costs plus installation labor, and material costs for electrical, piping, ductwork, foundations, structural, instrumentation, insulation, and site preparation.

TABLE 1-10. ESTIMATED AVERAGE ANNUAL REVENUE REQUIREMENTS FOR A 500 MW APPLICATION OF THE SFGT PROCESS[a]

Item	Annual quantity	Unit cost($)	Annual cost($)	% of annual revenue required
Direct Costs				
Raw materials				
NH_3	7.87x10^{6}kg	0.16512/kg	1,299,500	3.87
Naphtha	39,773 m^3	132.1/m^3	5,254,000	15.65
Catalyst	-	-	12,600,300	37.53
Reformer catalyst	-	-	125,100	0.37
Total raw materials			19,278,900	57.42
Conversion costs				
Operating labor and supervision	29,200 labor hrs	12.50/ labor hr	365,000	1.09
Utilities				
Naphtha	9,943 m^3	132.1/m^3	1,313,500	3.91
Steam	179,900 GJ	1.90/GJ	341,200	1.02
Process water	8,078,000 m^3	0.23/m^3	128,000	0.38
Electricity	68,859,000 kWh	0.029 kWh	1,996,900	5.95
Heat credit	1,047,500 GJ	-1.90/GJ	(1,896,000)	(5.65)
Maintenance			1,891,000	5.63
Analyses	4,380 labor hrs	17.00/labor hr	74,500	0.22
Total conversion costs			4,214,100	12.55
Total direct costs			23,493,000	69.97
Indirect Costs				
Capital charges				
Depreciation = (0.06)(total depreciable investment)			4,926,400	14.67
Average cost of capital = (0.086) (total capital investment)			7,238,800	21.56
Overheads				
Plant = (0.5) (conversion costs minus utilities)			1,165,300	3.47
Administrative = (0.1) (operating labor costs)			36,500	0.11
Marketing = (0.1) (sales revenue)			366,000	1.09
Total indirect costs			13,733,000	40.90
Spent catalyst disposal			11,400	0.03
Gross average annual revenue requirement			37,237,400	110.90
Byproduct Sales Revenue				
H_2SO_4	11.1 x 10^{6}kg	-0.033/kg	(3,660,000)	(10.90)
TOTAL ANNUAL REVENUE REQUIREMENTS			33,577,400	100.00

[a] Basis: 500 MW new coal-fired power plant 3.5% S coal. 90 percent NO_x reduction, 90 percent SO_2 removal. Midwest power plant location, 1980 revenue requirements. Remaining life of power plant = 30 years. Plant on line 7000 hr/yr. Plant heat rate equals 9.5 GJ/kWh. Investment and revenue requirement for disposal of fly ash excluded. Total direct investment $47,264,000; total depreciable investment $82,107,000; and total capital investment $84,172,000.

process. As shown, the average annual revenue requirement was estimated to be approximately \$33.6 x 10^6 which is equivalent to 9.60 mills/kWh. When compared to TVA's previous estimate of \$22.5 x 10^6/yr this represents almost a 50 percent increase in the annual revenue requirements for the process.

As with the capital costs, the principal factor which increased the annual revenue requirements is the increased quantity of acceptor required in the reactor. Additional acceptor as a raw material accounts for over 50 percent of the increase in annual revenue requirements. Another significant factor which increased annual revenue requirements is the estimated increase in naphtha required for hydrogen generation. This accounts for about 12 percent of the increase in annual revenue requirements.

Cost Comparison and Summary

The capital investment and annual revenue requirements of the SFGT process have been estimated based on the results of the test conducted at the EPA sponsored pilot plant in Tampa, Florida. The results of these cost estimates indicate that the capital costs and annual revenue requirements are higher than the estimated costs prior to the test program. A more important comparison, however, is the cost of the SFGT process relative to the cost of a conventional, NO_x only SCR process.

Since the same basis was used in preparing the modified SFGT cost estimate as TVA used in preparing preliminary economic estimates for other SCR processes, it is possible to make a direct comparison with TVA's previously published results. Table 1-11 presents the estimated annual revenue requirements for two pollution control systems which reduce emissions of particulates, NO_x and SO_2 by 99.5, 90 and 90 percent respectively. As shown, the pollution control systems employ two SCR processes tested by EPA, one being the SFGT process. The other SCR process is coupled with a flue gas desulfurization system and both processes have ESP's located downstream in order to put the cost estimates on a common basis.

TABLE 1-11. ESTIMATED ANNUAL REVENUE REQUIREMENTS FOR TWO POLLUTION CONTROL SYSTEMS[1]

SCR Process	Annual Revenue Requirements ($ x 10^{-6})			
	SCR	FGD	ESP	Overall
SFGT	33.6	-	3.0	36.6
Hitachi Zosen	10.2	14.7	2.2	27.1

[1] All costs except the SFGT-SCR and HZ SCR costs are from "Preliminary Economic Analysis of NO_x Flue Gas Treatment Processes". Tennessee Valley Authority - Office of Power. EPA - 600/7-80-021, February, 1980. HZ SCR costs are from "Independent Evaluation of the Hitachi Zosen NO_x Flue Gas Treatment Process". Radian Corporation - Draft Report. January, 1982.

As shown, in Table 1-11, the estimated costs associated with the SFGT processes are 35 percent higher than those of the pollution control system which employs the HZ SCR process. This indicates that the SFGT process, as tested in the pilot plant and presented in the conceptual design, is not competitive with a conventional NO_x only SCR process for the 500 MW application examined in this study. It should be noted, however, the relative costs presented in Table 1-11 are only valid for one specific application and they could change for other applications.

Overall the results of the modified cost estimate indicate that, for the particular application examined in this study, the costs of the SFGT process do no appear to be competitive with the costs of other SCR processes. This is based on the conceptual design which was limited to operating conditions demonstrated during the pilot plant tests. It is possible that estimated costs would change significantly for a design based on operating conditions which include the use of preoxidation and cooling. It is also possible that SFGT process costs may be more competitive with the costs of other SCR processes for lower sulfur coal applications.

A key factor in all the cost estimates is the useful life of the acceptor. For the estimates presented in this evaluation, a one-year life was assumed. If the acceptor life is longer or shorter than one year, costs could vary significantly from those estimated in this study. Further development work should focus on defining acceptor life and on demonstrating alternate operating/design conditions designed to minimize acceptor requirements.

1.4 CONCLUSIONS

The following discussion presents conclusions based on the work performed during this study. For the most part, the information obtained during the course of the study is summarized in this report and serves as background for the conclusions presented here. The major conclusions of this study are:

- The SFGT process can simultaneously reduce NO_x and SO_2 emissions by 90 percent when applied to a coal-fired boiler. However, this level of emissions reduction can only be attained at the expense of increased acceptor volume (over the pilot plant design) or through the use of operating and/or design options which were tested only for a short period during the pilot plant test program.

- No problems with reactor plugging or declinging acceptor activity were evident during the pilot plant test program. This indicates that the copper oxide acceptor and the parallel passage reactor design appear technically suited for application to a coal-fired source. The pilot plant tests did not, however, demonstrate a stable acceptor life equivalent to 1-year of commercial operation. While this was not an objective of the test program, it must be verified to establish the technical and economic feasibility of the process.

- The secondary emissions sampling program did not indicate any adverse environmental impacts would result from application of the SFGT process as operated during the pilot plant tests. However, the measured NH_3 emissions may not be representative of a full-scale application of the process.

- The secondary emissions sampling program did establish the fact that the SFGT process removes SO_3 from the flue gas. This represents a significant benefit for the process since removal of SO_3 permits recovery of additional heat in the air preheater. In addition, the low concentrations of SO_3 measured at the reactor outlet should preclude any problems with plugging and corrosion of a downstream air preheater due to the formation of ammonium sulfates.

- The conceptual design and material balance calculations indicated that significant increases (over TVA's preliminary estimate) in H_2, steam, and NH_3 consumption are expected based on the pilot plant test results. Of these, H_2 consumption has the greatest impact on the economic feasibility of the process. Since a detailed characterization of the factors which influence H_2 consumption was not completed during the pilot plant tests, it may be possible to reduce H_2 consumption. This represents an area which warrants further investigation.

- Nearly all of the potential heat credits available to the SFGT process can be recovered which results in reducing overall process energy requirements by about 40 percent.

- The overall energy balance indicated that the SFGT process has an energy requirement equivalent to 5 percent of the energy input to the boiler for a 500 MW application. When combined with an ESP, the SFGT process requires about 50 percent more energy than other SCR systems combined with ESP's and FGD systems. The principal component of the overall process energy requirement is the fuel energy associated with the naphtha used to generate hydrogen.

- The estimated total capital investment and average annual revneue requirements for the SFGT process are significantly higher than the costs for a conventional, NO_x only SCR process combined with an FGD system. This indicates that the SFGT process is not economically competitive with other SCR systems for the case examined as part of this evaluation. However, there are alternative applications of the SFGT process which may be more economically competitive. The alternatives include the use of preoxidation and cooling steps now recommended by UOP and applications of the process on sources firing low-sulfur coal.

Overall, the SFGT process design examined in this study does not appear economically competitive with a conventional, NO_x only SCR process for high sulfur coal applications. It may be more competitive for low sulfur coal applications, but this evaluation did not quantify costs for such an alternative. In addition, there are several techniques which could reduce overall process costs, but these were not examined in detail during the pilot plant test program.

SECTION 2

INTRODUCTION

Selective catalytic reduction (SCR) of NO_x with ammonia is capable of reducing NO_x emissions by 80 percent or more. As such, SCR represents the most effective process available for controlling stationary source NO_x emissions. For a utility application of SCR, a catalytic reactor is located between the economizer and air preheater sections of the boiler. At this point the flue gas temperature ranges from 300 to 400°C (570-750°F) which is suitable for the NO_x reduction reactions to occur rapidly. Ammonia is injected into the flue gas upstream of the catalyst and reacts with NO_x on the catalyst surface to form elemental nitrogen and water. The overall reactions can be represented by Equations 2-1 and 2-2.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{2-1}$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \tag{2-2}$$

The actual mechanism of NO_x reduction may be more complex than illustrated by these equations.

Most SCR processes were developed and are being operated commercially in Japan, primarily on gas and oil-fired sources. In a recent survey of SCR systems in Japan, they were found to be operating reliably at design levels and the operators reported that the catalyst life is exceeding vendor guarantees.[2] In the U.S., SCR systems are being installed on a limited basis. The most notable application is a demonstration system that is being constructed to treat one-half of the flue gas from Southern California Edison's 215 MWe Huntington Beach Unit No. 2 (an oil-fired boiler). The operation of this system is expected to establish SCR as a commercially available technology for oil and gas-fired sources in the U.S.

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In Japan, development efforts are now aimed at applying SCR to coal-fired sources. To date, many of the SCR process vendors in Japan have operated pilot units on slipstreams from coal-fired boilers. In addition, there are now four full-scale SCR systems treating flue gas from coal-fired boilers with another eight units scheduled for start-up in 1982 and 1983. These development efforts are rapidly establishing SCR as commercially available technology for controlling NO_x emissions from coal-fired sources in Japan.

The transfer of SCR technology from Japan to the U.S. for coal-fired applications presents a potentially significant problem. Since most coal-fired boilers in the U.S. operate ESP's located downstream of the air preheater, the catalyst in an SCR reactor would be exposed to the full particulate concentration from the boiler. And although tests have been conducted in Japan in which the catalyst was exposed to high particulate concentrations with no adverse effects, the differences in the composition of particulates from U.S. and Japanese coals could impact SCR operation.

In an effort to further the development of SCR technology and in particular to determine how differences between Japanese and U.S. coal/particulate properties impact the performance of SCR processes, EPA has sponsored pilot scale tests of two SCR systems. The SCR systems tested were the Hitachi Zosen (HZ) process and the Shell flue gas treating (SFGT) process, which is also capable of removing SO_2 from the flue gas. In both cases, the pilot plants processed a flue gas slipstream from a coal-fired boiler. The contractors responsible for the design and operation of these pilot plants were Chemico Air Pollution Control Corporation, which is the North America licensee for the HZ process, and the Process Division of UOP who is the licensing agent of the SFGT process. These contractors were also responsible for collection, evaluation, and reporting of the test data.

The EPA sponsored test programs were divided into the following four phases:

- Phase I - During this phase a detailed process design and a capital and operating cost estimate for the completed pilot plant were completed.
- Phase II - This phase consisted of procurement, fabrication, and erection of the pilot plant equipment followed by operator training, mechanical testing and procurement of raw materials required for testing.
- Phase III - This phase consisted of start-up and debugging of the pilot plant followed by variable tests to optimize performance of the plant.
- Phase IV - During this phase, each pilot plant was to be operated continuously for three months at optimum operating conditions. This period was to include no less than 75 days of cumulative operation in compliance with the contract objectives.

The primary objectives of the pilot plant test programs were (1) to demonstrate the ability of the processes to achieve a 90 percent reduction in NO_x emissions, and in the case of the SFGT process a simultaneous 90 percent reduction in SO_2 emissions and (2) to determine the impacts on catalyst performance which result from processing flue gas from a coal-fired utility boiler. Some secondary objectives of the test program included:

- determination of the effects of varying concentrations of SO_2 and NO_x on the processes performance,
- quantification of the processes raw material and utility requirements to permit an accurate estimate of operating costs for a full-scale SCR system,
- determination of optimum conditions for operation of each process, and
- characterization of process influent and effluent streams.

In conjunction with the pilot plant test program, EPA contracted Radian Corporation to prepare an independent evaluation of the processes tested based on the pilot plant results. This report presents the results of the independent evaluation of the SFGT process. A separate report was prepared which contains an evaluation of the HZ process.

Program Objectives and Approach

The independent evaluation conducted by Radian Corporation had three major objectives. The first was to provide independent validation of the process measurements made by UOP. The second objective was to quantify any changes in the emission rates of secondary pollutants across the pilot SCR reactor. And the third objective was to complete a technical evaluation of the SFGT process including identification of areas which require further development or investigation.

In order to validate the measurements made by UOP, a quality assurance program was implemented. This program used EPA reference methods and other standard measurement techniques to make independent audits of critical process parameters such as flue gas flowrate, NH_3 injection rate, etc. The results of these quality assurance audits were then compared to the process operators measurements and if the difference was greater than ten percent, an investigation was made to resolve the discrepancy.

In conjunction with the quality assurance program, the relative accuracy of the continuous NO_x and SO_2 monitors was determined by stack sampling using EPA reference methods. The monitors were also subjected to tests which measured two hour zero and calibration drift, calibration error, and response time. The results of these continuous monitor audits were then compared to the performance specifications for continuous monitor systems (CMS) applied to power plants which must comply with New Source Performance Standards (NSPS). If the pilot plant monitor audit results were outside the limits set by the CMS Performance Specifications, the cause was determined and the monitor was retested.

Concurrent with the quality assurance program, a stack sampling program was conducted to measure changes in secondary process emissions across the SCR reactor. This approach required simultaneous sampling of the reactor inlet and outlet for the species of interest. The samples were then analyzed and any differences in inlet and outlet concentrations determined.

Based on the results of the quality assurance program, the stack sampling program, and the test data collected by UOP, an evaluation of the SFGT process was completed. This evaluation consisted of several steps. First, the test data were analyzed and reduced to a form which could be used to predict process performance for a specified set of operating conditions. Then, using the reduced test data and the results of the stack sampling program, material and energy balance calculations were completed for a 500 MWe coal-fired application of the SFGT process. The basis for these calculations was identical to that used by TVA in developing cost estimates for the SFGT process as presented in "Preliminary Economic Analysis of NO_x Flue Gas Treatment Processes".[1] The material and energy balance calculations developed from the pilot plant data were then compared to those developed by TVA and a modified cost estimated based on the pilot plant test results was developed. Finally, the test data were reviewed and areas requiring further investigation/quantification were identified.

Report Organization

This report presents the results of the evaluation of the SFGT process. Section 3 contains a description of the pilot plant including flue gas composition, flowrates, etc. In addition, it contains a summary of the test plans followed by UOP and Radian. Section 4 summarizes and interprets the results of both the pilot plant tests and the sampling programs conducted by Radian. (A more detailed presentation of Radian's test results appear in the Appendices). Section 5 presents the results of the material and energy balance calculations and the modified cost estimate for a 500 MW application of the SFGT process. In Section 6, areas requiring further investigation or development work are identified.

SECTION 3

FIELD TEST PROGRAM

In May 1978, EPA issued a contract to the Process Division of UOP for the design, construction and operation of a pilot plant capable of simultaneously reducing SO_2 and NO_x emissions by 90 percent. The design and construction phase of this project involved modification of an existing pilot unit which had been used to test the SFGT process for SO_2 removal. This phase of the program was essentially completed in June 1979. The next phase of the project included start-up and debugging, and this was completed in October 1979. Optimization tests were then conducted throughout a 1-year period which ended in October 1980. During June, July, and August 1980, the demonstration phase of the program was conducted. In June and July 1980, Radian Corporation conducted its quality assurance and stack sampling test programs.

This section presents details of the test programs conducted by UOP and Radian Corporation. Included as background is a general discussion of the SFGT process and a specific description of the pilot plant with details of plant instrumentation and process flows.

3.1 THE SFGT PROCESS

The SFGT process is a unique SCR process since it is capable of reducing NO_x while simultaneously removing SO_2 from a flue gas stream. This process employs copper, supported on aluminia as the active material (termed the "acceptor") in the NO_x reduction and SO_2 removal reactions. When the acceptor is exposed to a gas stream containing O_2, SO_2, NO_x and NH_3, the following reaction sequence can occur. First, the elemental copper reacts with oxygen to form copper oxide as illustrated by Equation 3-1.

$$Cu(s) + \frac{1}{2}O_2(g) \rightarrow CuO(s) \qquad (3\text{-}1)$$

The copper oxide can then react with and remove (accept) SO_2 from the gas stream as illustrated in Equation 3-2.

$$CuO(s) + SO_2(g) + \frac{1}{2}O_2(g) \rightarrow CuSO_4(s) \qquad (3\text{-}2)$$

In the presence of NH_3, both copper oxide and copper sulfate catalyze the reduction of NO_x. The overall reactions for NO_x reduction are illustrated by Equations 3-3 and 3-4.

$$4NO(g) + 4NH_3(g) + O_2(g) \rightarrow 4N_2(g) + 6H_2O(g) \qquad (3\text{-}3)$$

$$2NO_2(g) + 4NH_3(g) + O_2(g) \rightarrow 3N_2(g) + 6H_2O(g) \qquad (3\text{-}4)$$

The gas temperature required for all of these reactions to occur rapidly is approximately 400°C. Some additional reactions which can occur in an SFGT reactor include the oxidation of NH_3 (Equation 3-5) and the removal of sulfur trioxide (Equation 3-6).

$$4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(g) \qquad (3\text{-}5)$$

$$CuO(s) + SO_3(g) \rightarrow CuSO_4(s) \qquad (3\text{-}6)$$

As the copper oxide reacts with SO_2 and SO_3, the acceptor gradually becomes sulfated and thus looses its ability to remove SO_2 from the flue gas. Once the acceptor becomes sulfated beyond a level consistent with design SO_2 removal requirements, regeneration is necessary. Conveniently, the acceptor can be regenerated at 400°C using a reducing gas (e.g., H_2, CO, CH_4, etc.). The choice of reducing gas is an economic one but for discussion purposes it will be assumed that H_2 is used. There are three reasons for this assumption: (1) H_2 was used as the reducing in the pilot plant tests, (2) TVA used H_2 as the basis for their cost estimate for the SFGT process, and (3) H_2 appears well suited for use in most utility situations.

Regeneration of the sulfated acceptor occurs when exposed to a dilute stream of H_2 at 400°C. The overall regeneration reaction can be illustrated by Equation 3-7.

$$CuSO_4(s) + 2H_2(g) \rightarrow Cu(s) + SO_2(g) + 2H_2O\ (g) \qquad (3\text{-}7)$$

This reaction occurs very rapidly and it moves in a "front" through the reactor. After regeneration, the acceptor is primarily elemental copper and is thus capable of removing SO_2 from the flue gas again.

Regeneration of the acceptor produces an off gas stream consisting of SO_2 and H_2O. During the pilot plant tests this stream was simply vented to the boiler's stack but in commercial operation it can be further processed to recover the SO_2 as sulfuric acid or elemental sulfur.

Aside from the basic chemistry discussed above, the actual design of an SFGT process can vary from application to application depending on specific pollution control requirements and the characteristics of the process being controlled. The discussion presented here will focus on one particular design which is well suited to a utility application of the process and in particular to coal fired boilers. This design employs a parallel passage, fixed bed reactor to process flue gas for pollutant removal. In the parallel passage reactor, flue gas flows through open channels parallel to the acceptor material. This design is well suited to particulate laden gas streams since the particulates can flow through the open channels without plugging the catalyst bed. This same design provides effective exposure of the acceptor to the flue gas which permits the SO_2 removal and NO_x reduction reactions to occur rapidly.

The use of a fixed bed reactor results in a cyclic process which consists of an acceptance period and a regeneration period. The reactor processes flue gas during acceptance and then is removed from the flue gas stream after the bed is sulfated. The sulfated bed is regenerated and is then available for processing flue gas again. Before and after the reactor is regenerated it is purged with steam to prevent combustion of the reductant in the freshly regenerated reactor.

The cyclic nature of a fixed bed process also results in a unique pattern of off gas concentrations over an acceptance period. Figure 3-1 illustrates typical reactor outlet concentrations of NO_x and SO_2 over the duration of an acceptance period. As shown, the SO_2 concentration at the reactor outlet drops rapidly at the start of an acceptance period as the Cu is converted to CuO which can then react with SO_2. The outlet concentration then gradually increases over the acceptance period as the bed becomes sulfated. The outlet NO_x concentration is also very high initially. As the bed is oxidized, NO_x removal begins and increases continually over the length of the acceptance period. This continual increase is due to several factors including conversion of CuO to $CuSO_4$ which is a more effective catalyst for the NO_x reduction reactions.

If continuous processing of the flue gas is required (e.g., a boiler required to reduce SO_2 emissions by 90 percent), two or more reactors are needed. During the regeneration of one reactor, one or more reactors continue to process flue gas. Once the regeneration is complete, the reactor can be returned to service and another reactor regenerated. Since the flow of regeneration off gas is intermittent, it may be necessary to route it through a flow smoothing system (e.g., a pressurized tank) prior to processing for sulfur recovery. Flow smoothing would be required in a situation where the only feed source for the sulfur recovery process is the SFGT process. This would be the case for most utility applications.

3.2 SFGT PILOT PLANT DESCRIPTION

The SFGT pilot plant was located at the Big Bend station of the Tampa Electric Company. The plant was originally constructed in 1974 and revamped for the EPA test program in 1979. Flue gas for the pilot plant was withdrawn from between the economizer and the air preheater of the coal-fired unit No. 2. The flue gas composition at this point is presented in Table 3-1. As shown, the particulate concentration was representative of the full particulate loading from the boiler.

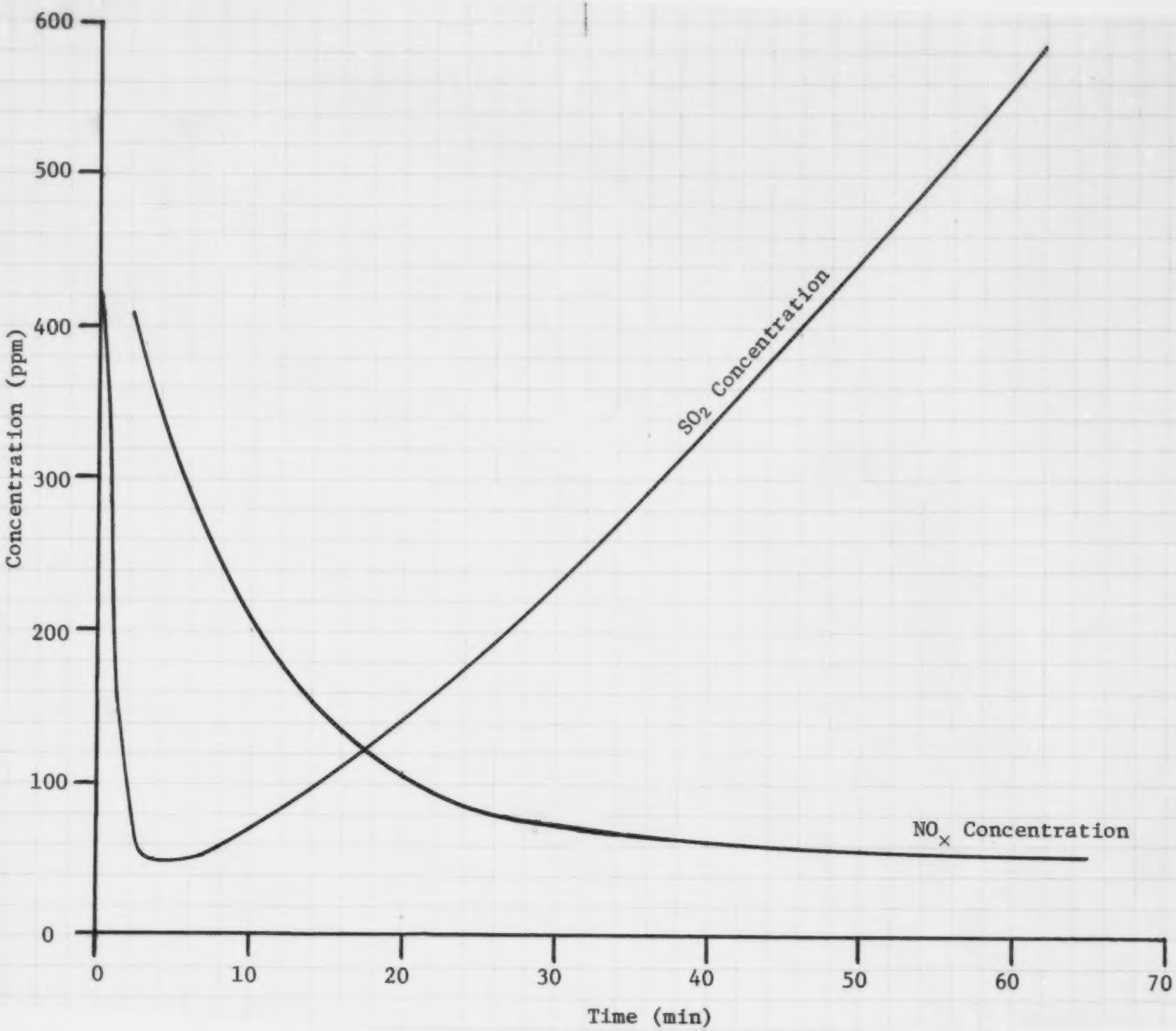

Figure 3-1. Typical SO_2 and NO_x concentrations at the SFGT reactor outlet.

TABLE 3-1. COMPOSITION OF FLUE GAS ENTERING THE SFGT PILOT PLANT

Component	Concentration
N_2	65.4%
CO_2	16.3%
O_2	4.5%
H_2O	13.8%
Particulates	7.6 gm/dscm

The flue gas flowrate through the pilot plant was approximately 1610 Nm^3/hr (1000 scfm) which is equivalent to approximately 0.5 MW of electric generating capacity.

Figure 3-2 is a schematic of the SFGT pilot plant. Flue gas from unit No. 2 was compressed by a flue gas fan and then passed through several propane fired flue gas heaters before entering the reactor. The main heater was designed to replace heat lost in the ducts between unit 2 and the pilot plant while two trim burners were included to provide a controlled temperature at the entrance to the reactor. After exiting the trim burners the flue gas could either continue into the reactor or be diverted through a by-pass loop. The by-pass loop contained a control valve which was operated to provide constant flow to the reactor during the acceptance period.

NH_3 was injected into the flue gas just upstream of the reactor and just downstream of a venturi which was used to measure the reactor feed rate. The gas then flowed up through the reactor which contained a 6- or 7-meter stack of acceptor. This stack was comprised of "unit cells" of acceptor material each of which was 1 meter deep by 0.25 m^2. The reactor design included a gas distributor upstream of the first cell of acceptor and electric heaters to permit adabatic operation (i.e., to make up for heat loss to the surroundings). In addition, valves were located at the entrance and exit of the reactor so it could be isolated during regeneration. Flue gas exiting the reactor was returned to the main boiler duct.

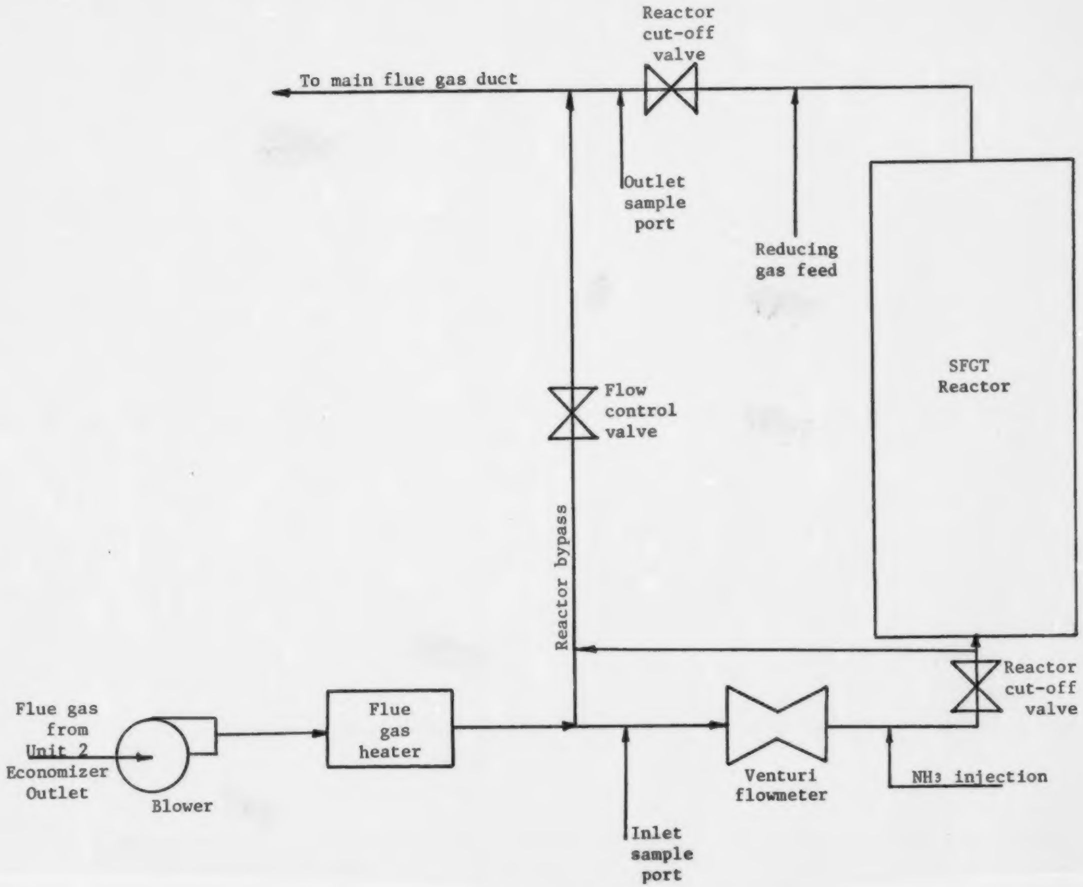
Reactor cut-off valve
To main flue gas duct
Outlet sample port
Reducing gas feed
SFGT Reactor
Flow control valve
Reactor bypass
Flue gas from Unit 2 Economizer Outlet
Blower
Flue gas heater
Inlet sample port
Venturi flowmeter
NH_3 injection
Reactor cut-off valve

Figure 3-2. Schematic of the SFGT pilot plant.

As shown in Figure 3-2, the SFGT pilot plant had only one reactor. Consequently, the pilot unit was only capable of treating flue gas intermittantly. When the reactor required regeneration, valves at the reactor inlet and outlet were closed and all the flue gas was diverted through the by-pass loop. The reactor was then purged with steam. Subsequently, reducing gas consisting of a mixture of superheated steam and H_2 was fed to the top of the reactor. The regeneration off gas, which contained SO_2 and steam, exited the bottom of the reactor. The flowrate and composition of this stream was measured before it was mixed with the flue gas in the reactor by-pass and returned to the boiler duct. During acceptance, the shut-off valve on the regeneration off gas line was closed but the valve on the reducing gas feed line was open and superheated steam was added to the flue gas exiting the reactor. This permitted continuous (and more reliable) operation of the boiler used to generate steam for the pilot unit. H_2 flow was terminated during acceptance and initiated only after the reactor was purged prior to regeneration. The reactor was also purged following regeneration to remove any residual H_2.

Table 3-2 identifies the instrumentation which was used to characterize the operation of the SFGT pilot plant. It should be noted that the information in Table 3-2 is not a complete list of the pilot plant's instrumentation. It does, however, identify those instruments used to quantify the plant's performance. As shown, instruments were installed to measure the quantity of materials entering and exiting the reactor during both the acceptance and regeneration periods. This permitted UOP to complete material balance calculations for SO_2 across the reactor. It also defined process requirements for raw materials such as H_2 and NH_3 and energy demands for steam and the power required by the fan to overcome the reactor pressure drop.

Two instruments which were included in the original pilot plant design but not shown in Table 3-2 are a continuous NH_3 analyzer to monitor NH_3 emissions from the reactor and an oxygen monitor. These instruments are not

TABLE 3-2. INSTRUMENTATION ON THE SFGT PILOT PLANT[1]

Parameter Measured	Measurement Location	Instrument
Flue Gas		
• Flowrate	Reactor Inlet	Venturi-FRC[2]
• Composition		
- NO_x	Reactor Inlet/Outlet	TECO 10A-Chemiluminescent
- SO_2	Reactor Inlet/Outlet	DuPont 460-Photometric
• Temperature	Reactor Inlet/Outlet Exit of Each Cell	Thermocouples
• Pressure	Reactor Inlet	Pressure Gauge
Steam		
• Flowrate	Regeneration Feed	Orifice-FRC[2]
• Pressure	Regeneration Feed	Pressure Gauge-PI[3]
• Temperature	Regeneration Feed	Thermocouple
H_2 Flowrate	Regeneration Feed	Orifice-FRC[2]
NH_3 Flowrate	Reactor Feed	Orifice-FRC[2]
Regeneration Off-Gas		
• Flowrate		Orifice-FRC[2]
• Composition		
• - SO_2		DuPont 460/TOF-MS[4]
• - H_2		TOF-MS[4]
Reactor Pressure Drop		Differential Pressure Cell

[1] This does not represent a complete instrument list

[2] FRC - Flow Recorder-Controller

[3] PI - Pressure Indicator

[4] TOF-MS - CVC Time of Flight Mass Spectrometer

shown in the instrument list because they were inoperative during the pilot plant tests. In the case of the NH_3 monitor, UOP made a significant effort to operate this instrument but the readings were erratic when analyzing flue gas. As a consequence, the only measure of NH_3 emissions was made by periodic batch sampling and wet chemical analysis. The O_2 monitor was not operated since its maintenance was considered secondary to the maintenance requirements of the SO_2 and NO_x monitors. As a result, the concentration of SO_2 and NO_x at the reactor inlet could not be corrected to a specific O_2 level or expressed as mass emission rate (e.g., ng/J). However, since the reactor did operate under positive pressure, no dilution occurred and the pollutant concentrations at the reactor inlet and outlet were on the same basis.

3.3 SFGT PILOT PLANT TEST PROGRAM

The test program at the SFGT pilot plant was initiated in October 1979, and was completed in October 1980. This program involved examination of 3 charges of acceptor material under a variety of test conditions including tests for simultaneous reduction of NO_x and SO_2 emissions and tests for removal of only NO_x or SO_2. In general, these tests can be divided into two categories: optimization tests and demonstration or long-term tests. The objective of the optimization tests was to identify operating conditions which would reduce both NO_x and SO_2 emissions by 90 percent at a minimum total cost for operating the process. The objectives of the demonstration tests were: (1) to document the ability of the process to achieve 90 percent reduction in NO_x and SO_2 emissions over a long period of time, and (2) to accurately quantify the process' raw material and utility requirements at operating conditions which produced 90 percent reduction in NO_x and SO_2 emissions. The following discussion presents a brief operating history of the SFGT pilot plant including a discussion of each batch of acceptor tested. Section 4 presents a detailed discussion and interpretation of test results.

3.3.1 Optimization Tests - Philosophy

The optimization tests conducted by UOP were divided into two groups: clean system tests and flue gas tests. In the clean system tests, the pilot plant processed a simulated flue gas stream which consisted of heated air with NO and/or SO_2 injected. These tests were included in the program to establish a basis for comparison of plant performance with and without particulates present. In the flue gas tests, the plant operated normally, processing hot, particulate laden gas from the economizer outlet of Unit 2. These tests were designed to examine the effects of process operating parameter levels on the performance of the SFGT pilot plant.

The principal variables examined in both the clean system and flue gas optimization tests were:

- Flue Gas/Reactor Temperature,
- Flue Gas Flowrate,
- Acceptance Time
- NH_3/NO_x Injection Ratio,
- NH_3 Injection Delay Time,
- Fraction of Acceptor Regenerated, and
- Preoxidation of Acceptor.

The effect of each of these variables on the performance of the SFGT process can vary in magnitude and direction. The following discussion briefly examines each variable and identifies its directional impact on both NO_x and SO_2 reduction efficiencies.

Flue Gas/Reactor Temperature

The temperature at which the SFGT reactor operates can affect both the NO_x reduction and SO_2 removal rates. As the reactor operating temperature increases, the rate of the NO_x and SO_2 reduction rates will increase due to an increase in the chemical reaction rate and/or diffusion rate. However, beyond a certain temperature, the rate of NO_x reduction will begin to decrease. This is due to an increase in the rate of a secondary reaction in which NH_3 is oxidized to form NO_x. At the temperature where the increased rate of the NO_x reduction reaction is offset by increased NH_3 oxidation, the NO_x reduction rate can be maximized.

Flue Gas Flowrate

Changes in flue gas flowrate will impact both NO_x reduction and SO_2 removal of the SFGT process. In the case of SO_2, an increase in flowrate will decrease time averaged removal efficiency for a fixed acceptance time. Since the quantity of acceptor is fixed, an increase in flue gas flowrate means that more SO_2 is fed to the reactor and thus, the acceptor becomes sulfated more quickly. As a consequence, at a specific time in an acceptance period (e.g., 50 min) the SO_2 emissions will be greater at higher flowrates. The impact of changing flue gas flowrate on NO_x removal is less obvious. Under some operating conditions an increase in flowrate will result in an increase in NO_x reduction efficiency and under other conditions, the NO_x reduction efficiency would be expected to decrease.

Acceptance Time

For a specific reactor design (i.e., a fixed quantity of acceptor) the acceptance time has a significant and opposite effect on the NO_x and SO_2 reduction efficiencies of the SFGT process. As acceptance time increases, both instantaneous and time averaged SO_2 removal efficiencies decrease while NO_x reduction efficiencies increase. The SO_2 removal efficiency decreases due to the progressive sulfation of the acceptor which results in higher instantantaneous and time averaged SO_2 emissions. The continued increase in NO_x reduction efficiency is due in part to an increase in the quantity of $CuSO_4$

available as catalyst. However, at a certain time in the acceptance period, the instantaneous NO_x reduction reaches a steady state level beyond which little improvement occurs. Yet, increased acceptance times continue to improve the time averaged NO_x reduction efficiency. This is due to the fact that most of NO_x emissions occur early in an acceptance period and in general these emissions are not dependent on the length of the acceptance period. As a consequence, longer acceptance periods result in lower time averaged NO_x emissions.

NH_3/NO_x Injection Ratio

The NH_3/NO_x injection ratio is a key variable in determining the NO_x reduction efficiency in the reactor. At an NH_3/NO_x ratio less than 1.0, an increase in the injection ratio produces a corresponding increase in NO_x removal. As the ratio is increased above 1.0, NO_x reduction efficiency will asymptotically approach a limiting value. Finally, further increases in the injection ratio do not produce any change in reduction efficiency. In the case of the SFGT process, the limiting value for the time averaged NO_x reduction efficiency will depend on the NO_x slip during the initial part of an acceptance period and on the length of the acceptance period. Assuming the reactor is large enough, the limiting value for the instantaneous NO_x reduction efficiency is 100 percent.

NH_3 Injection Delay Time

Delay of NH_3 injection at the start of an acceptance period can change the time averaged NO_x reduction efficiency. Depending on operating conditions and the length of the delay, an increase or decrease in reduction efficiency can result. An increase in reduction efficiency may result from a short delay since, at the initiation of an acceptance period, the acceptor has a tendency to promote oxidation of NH_3 to NO_x and thus increase the initial NO_x slip. However, longer delays in initiating NH_3 injection can result in decreased NO_x reduction since less ammonia is available for reaction with NO_x at the start of acceptance. It may, therefore, be possible to improve the NO_x reduction efficiency by optimizing the NH_3 injection delay.

Fraction of Acceptor Regenerated

The fraction of sulfated acceptor which is regenerated can influence both the NO_x reduction and SO_2 removal efficiencies of the SFGT process. If less than 100 percent of the acceptor is regenerated, some sulfated acceptor will be present at the start of an acceptance period. With all other process operating parameters constant, an increase in the quantity of sulfated acceptor present at the start of an acceptance period should result in a decrease in the time averaged SO_2 removal efficiency and an increase in the time averaged NO_x reduction efficiency of the process. SO_2 removal will decrease since there is less CuO available for reaction while NO_x reduction should increase since some acceptor will be catalytically active from the start of the acceptance period. This is not the case if all the acceptor is converted to elemental copper during regeneration.

Preoxidation of the Acceptor

Another means of making the acceptor catalytically active at the start of an acceptance period is to include a preoxidation step between regeneration and acceptance. Preoxidation would convert the acceptor from elemental copper to the copper oxide form which is an active catalyst for the NO_x reduction reactions. This should result in a decrease in the initial NO_x slip and an overall increase in the time averaged NO_x reduction efficiency. Preoxidation may also produce an improvement in SO_2 removal efficiency since the acceptor will not have to be oxidized before the SO_2 removal reaction will proceed.

Summary

As evident from the preceding discussion the process operating variables can interact in a complex manner to produce changes in the NO_x reduction and SO_2 removal efficiencies of the SFGT process. It was the objective of the optimization tests to examine the impact of each variable on process performance and thereby identify operating conditions which resulted in the simultaneous reduction in the emission rates of NO_x and SO_2 by 90 percent. In practice, each variable was examined separately and the optimum level determined. In some cases the variables had little or no effect on process performance and so the optimum level was that which maximized throughput or minimized process raw material and utility requirements. The following discussion presents a brief history of the optimization tests while Section 4 summarizes the most significant results of both the optimization and demonstration tests.

3.3.2 Optimization Tests - History

Optimization tests were conducted for each of the three charges of acceptor material installed in the SFGT pilot plant, while long-term or demonstration tests were only conducted with the second charge of acceptor. The following discussion summarizes the optimization tests conducted on each charge of acceptor. This includes a summary of the total time flue gas was processed by each acceptor.

Acceptor 1

The first acceptor charge for the SFGT pilot plant was loaded into six "unit cells" and it contained approximately 330 gram moles of copper. After start up and debugging, optimization tests were initiated in October 1979. During the initial tests the reactor processed air with injected pollutants. The variables examined in these tests are shown in Table 3-3 along with the optimum values defined by the tests. At the "optimum" conditions, NO_x and SO_2 reduction efficiencies were 94.8 and 89.8 percent respectively.

TABLE 3-3. OPTIMIZATION TEST RESULTS FOR ACCEPTOR 1[1]

Variable Tested	Optimum Level
Flue Gas/Reactor Inlet Temperature	400°C
Reynolds Number (Flue Gas Flowrate)	2000 (1600 Nm^3/hr)
NH_3/NO_x Injection Ratio	1.1
NH_3 Injection Delay Time	2 min.

[1] During these tests acceptance time was constant at 100 min and the regeneration time at 30-35 min.

Flue gas tests were initiated for the first time in December 1979. During this month, the plant processed flue gas for a total of 147 hours. At the operating conditions defined in Table 3-3, NO_x and SO_2 reduction efficiencies were 74 and 81 percent respectively. This represented a significant decline from the clean system test results and was below the project objective of a simultaneous reduction in NO_x and SO_2 emissions of 90 percent. Additional clean systems tests were conducted to check the activity of the acceptor, and it had declined between mid-October and late November. During this period it was suspected that the acceptor had been damaged from accidental exposure to liquid water and high oxidation temperatures. As a consequence, the decision was made to replace the acceptor with a fresh batch.

Acceptor 2

A second charge of acceptor, essentially identical to the first was placed in the reactor in January 1980. This charge was also loaded into six "unit cells" and it contained approximately 300 gram moles of copper. Over the next three months (February-April) a variety of clean system and flue gas optimization tests were conducted and flue gas was processed for about 250 hours. This included tests in which only SO_2 was removed (no NH_3 injection), only NO_x was reduced (no regeneration of the acceptor), and emissions of both NO_x and SO_2 were reduced.

Initial results of the optimization tests indicated performance similar to that of the first acceptor prior to its replacement. However, following an initial exposure to flue gas, the acceptor's activity declined. This was evidenced by a decline in SO_2 removal efficiency from 85 to 75 percent measured at the "optimum" conditions shown in Table 3-3. Apparently, exposure to fly ash resulted in an initial drop in the activity of the acceptor.

The variables examined during the optimization tests of the second acceptor included those shown in Table 3-3 and in addition, the length of the acceptance period (acceptance time). By decreasing the acceptance time it was possible to improve the SO_2 removal efficiency of the pilot unit although the NO_x reduction efficiency was reduced. Some typical results of these optimization tests are presented in Table 3-4. As shown, the reduction in NO_x and SO_2 emission rates was still below the program target of 90 percent reduction for both pollutants.

TABLE 3-4. TYPICAL RESULTS OF OPTIMIZATION TESTS ON ACCEPTOR 2.

Variable	Level
Flue Gas/Reactor Inlet Temperature	400°C
Reynolds Number (Flowrate)	2000 (1600 Nm^3/hr)
NH_3/NO_x Injection Ratio	1.5
NH_3 Injection Delay	0 min.
Acceptance Time	70 min.
SO_2 Removal	86%
NO_x Reduction	<75%

Based on the test results shown in Table 3-4, it was decided to add a seventh cell of acceptor to the reactor. During May 1980, the reactor was unloaded, the existing acceptor was screened to remove fly ash, and the reactor was reloaded with six cells of used acceptor and a single cell of fresh acceptor. At this point, the copper inventory in the reactor was approximately 390 gram moles (130 percent of the previous acceptor charge). Additional clean system and flue gas optimization tests were then conducted and flue gas was processed for about 150 hours. However, the plant was still unable to meet the objective of reducing both NO_x and SO_2 emissions by 90 percent. At this point it was decided to initiate a series of "demonstration" tests with modified objectives so no further optimization tests were conducted. During optimization tests on the second acceptor, flue gas was processed in the reactor for a total of 400 hours.

Acceptor 3

Because the second acceptor was unable to meet the program performance objectives, a third charge of acceptor was placed in the reactor in September 1980. This charge of acceptor was produced by UOP (the first and second charges were produced by Shell Chemical) and was expected to be more active than the previous charge. The acceptor was loaded into six unit cells and it contained approximately 470 gram moles of copper. This compares to 390 gram moles in the previous charge which represents a 21 percent increase in total copper inventory, and a 40 percent increase in the copper loading per unit cell.

Clean system tests were initiated in September 1980. The initial reduction in NO_x and SO_2 emissions was 80 and 96 percent respectively. Flue gas was then processed in the reactor and NO_x/SO_2 reduction efficiencies declined to 84 and 88 percent. After further flue gas optimization tests NO_x and SO_2 emission reductions of 81 and 90 percent were achieved at the conditions shown in Table 3-5. While this was still below the program performance objective, it was the best performance recorded to date.

TABLE 3-5. TYPICAL OPERATING CONDITIONS DURING ACCEPTOR 3 OPTIMIZATION TESTS.

Variable	Level
Flue Gas/Reactor Inlet Temperature	400°C
Reynolds Number (Flue Gas Flowrate)	2000 (1600 Nm^3/hr)
NH_3/NO_x Injection Ratio	1.2
NH_3 Injection Delay Time	0 min.
Acceptance Time	85 min.

Additional clean system and flue gas optimization tests were then conducted. During these tests, the sulfur content of the fuel fired in Unit 2 was reduced with a corresponding reduction of the SO_2 concentration in the flue gas from 2400 ppmv to 2000 ppmv. This resulted in an improvement in SO_2 removal at an acceptance time of 85 minutes. It was then possible to extend the acceptance time to 95 minutes and still achieve a 90 percent reduction in SO_2 emissions. Extending the acceptance time resulted in a 1 to 3 percent improvement in the NO_x reduction efficiency of the process.

During subsequent testing, a preoxidation step was included between regeneration and acceptance. This preoxidation step did not produce a significant improvement in NO_x reduction efficiency and the NO_x slip at the start of the acceptance period was still quite high. This high initial slip was believed to be due to oxidation of NH_3 which was promoted by the high (550°C) temperatures of the reactor internals that resulted from the exothermic copper oxidation reaction. In order to reduce the temperature of the reactor internals, a cooling purge was initiated after preoxidation but prior to acceptance. Employing these techniques at the operating conditions shown in Table 3-6, simultaneous reduction of NO_x and SO_2 emissions was at the 90 percent level for 8 acceptance periods. At this point, the UOP acceptor had processed flue gas for a total of 265 hours.

TABLE 3-6. OPERATING CONDITIONS FOR 90% NO_x/SO_2 REMOVAL

Variable	Level
Flue Gas/Reactor Inlet Temperature	395°C
Reynolds Number (Flue Gas Flowrate)	2000 (1690 Nm^3/hr)
NH_3/NO_x Injection Ratio	1.2
Acceptance Time	99 min.
Cooling Purge Time	66-90 minutes

In subsequent tests, the SO_2 removal began to decline due to an increase in the flue gas SO_2 concentration to 2400 ppmv. This indicated that 90 percent NO_x/SO_2 reduction could only be attained at a fixed molar flowrate of SO_2 to the reactor equivalent to 2000 ppmv SO_2 at 1600 Nm^3/hr (approximately 2.4 gram moles SO_2/min). Therefore, in order to maintain 90 percent NO_x/SO_2 reduction at an increased SO_2 concentration, it was necessary to reduce the flue gas flowrate and thus the molar flowrate of SO_2. This resulted in simultaneous reduction of NO_x and SO_2 emissions by 90 percent at the conclusion of the pilot plant test program. When the program ended, the third acceptor had processed flue gas for 375 hours and the pilot plant had processed flue gas for approximately 2000 hours with all three acceptors.

3.3.3 Demonstration Tests - Philosophy

One of the principal goals of the EPA sponsored SCR pilot plant test program was to complete a demonstration test of the SFGT process. The objectives of this demonstration test were (1) to operate the pilot plant continuously for 90 days including 75 days of operation at 90 percent reduction of both NO_x and SO_2, (2) to determine the long-term impacts of flue gas from a coal-fired boiler on the performance of the acceptor material, and (3) to quantify process raw material and utility requirements. As evident from the preceding discussion of the optimization tests, the first two objectives were not met during the test program. It was only in the final two weeks of testing that the plant was able to achieve 90 percent reduction in NO_x and SO_2 emissions while processing flue gas, and the longest total operating time for a single acceptor was equivalent to less than 3 months of commercial operation.

Because of the difficulty in meeting the program performance objectives, the objectives of the demonstration test were modified and demonstration tests were conducted with the second acceptor. The modified objectives called for the demonstration test to be divided into two phases. In the first phase, the objective was to operate under conditions which resulted in an SO_2 removal efficiency of 90 percent. The maximum NO_x reduction efficiency was limited to that attainable at an NH_3/NO_x injection ratio of 1.25. In the second phase of the demonstration test, the pilot plant was operated as a typical SCR process without regeneration and without removing SO_2 from the flue gas. The objective of this phase of the test was to achieve a 90 percent reduction in NO_x emissions without constraints on the NH_3/NO_x injection ratio.

The following discussion summarizes the demonstration tests conducted at the SFGT pilot plant. A more detailed discussion of the test results is presented in Section 4 of this report.

3.3.4 Demonstration Tests - History

The modified demonstration tests of the SFGT pilot plant were initiated in June and completed in August 1980. The first phase of these tests began on June 13 and included 22 days of operation. A minimum of 75 percent of the removal data was collected for 17 of the 22 operating days. For 5 of the days data capture was less than 75 percent due primarily to sample line/analyzer problems. Consequently, these data were not included in determining the pilot plant's compliance with the objectives of the demonstration test.

For the 17 "compliance" days, SO_2 removal averaged 90.4 percent while NO_x reduction efficiency averaged 69.0 percent. Average operating conditions which resulted in these reduction efficiences are shown in Table 3-7. For the 22 operating days in the demonstration test, flue gas was processed for 323 hours and a total of 293 acceptance periods.

TABLE 3-7. AVERAGE OPERATING PARAMETER LEVELS DURING THE DEMONSTRATION TEST FOR 90 PERCENT SO_2 REMOVAL

Operating Parameter	Level
Flue Gas/Reactor Inlet Temperature	412°C
Flue Gas Flowrate	1590 Nm^3/hr
NH_3/NO_x Injection Ratio	1.24
Acceptance Time	62.8 min

The principal variable used to maintain 90 percent SO_2 removal efficiency was the acceptance time which averaged $\sim$63 minutes. At the start of the demonstration test, acceptance time was 70 minutes but had to be reduced to maintain SO_2 reduction efficiency at 90 percent. Initially, this was thought to be a result of a decline in the activity of the acceptor, but subsequent tests indicated that acceptor activity was essentially unchanged at the completion of the demonstration test. The decline during the demonstration test was due, in part, to an unrecorded increase in flue gas flowrate.

The second phase of the demonstration test was initiated on July 9 and concluded on August 18. During this period, pilot plant operation was interrupted several times by boiler outages which resulted in a total of 35 operating days being recorded. Of the 35 operating days, a minimum of 75 percent of the data was collected for 31 days. During the 31 compliance days, the NO_x removal averaged 89.5 percent at an average NH_3/NO_x injection ratio of 1.26, a flue gas flowrate of 1600 Nm^3/hr, and a reactor inlet temperature of 416°C. Flue gas was processed for approximately 1000 hours during the 35 operating days and the plant performance was steady throughout this period.

The principal variable used to control the NO_x reduction efficiency during the second phase of the demonstration test was the NH_3/NO_x injection ratio. It was found that NO_x reduction was very sensitive to the NH_3/NO_x ratio in the range 1.2 to 1.3. This made it difficult to control NO_x removal precisely. As a result, the test objective of 90 percent NO_x reduction efficiency was not technically achieved. However, of the NO_x reduction data recorded, 58 percent was at or above the 90 percent level. If UOP had not exercised careful control over the NH_3/NO_x injection ratio it would have been possible to meet the test objective of 90 percent NO_x reduction at the expense of increased NH_3 usage.

3.4 INDEPENDENT EVALUATION TEST PROGRAM

As part of the independent evaluation of the SFGT process, Radian Corporation conducted a test program at the pilot plant. This program consisted of the following three elements:

- Quality Assurance Audits
- Secondary Emissions Sampling
- Continuous SO_2 and NO_x monitor certification

Overall, the objectives of this program were to validate the process measurements being made on a routine basis by UOP and to quantify any changes in the emission rates of secondary pollutants from the SFGT process. The test program and the individual program elements were designed to meet those objectives to provide input for the independent evaluation of the SFGT process.

The independent evaluation test program was conducted during June and July 1980, which coincided with the demonstration tests on the second acceptor. Individual test program elements were not conducted sequentially, but were intermeshed to make most efficient use of the field test crew. Quality assurance audits were conducted on a periodic basis, while the certification tests and the secondary emissions sampling were conducted simultaneously.

The following discussion presents specific details of the test plans which were followed for each of the program elements. Results of the independent test program are presented in Section 4 and in the appendices.

3.4.1 Quality Assurance Audits

Quality assurance audits were included as an element in the independent evaluation test program to insure the accuracy of the process measurements made on a routine basis by UOP. Not all process measurements were subject to audit. Only those measurements which are most significant in terms of quantifying the raw material and utility requirements were audited.

Table 3-8 identifies the process measurements which were subjected to audits along with the initial audit frequences. As shown, these process measurements represent the most basic operating parameters required to characterize the SFGT process. The principal raw material requirements are characterized by the quantity of NH_3 needed to reduce a specific quantity of NO_x and the quantity of H_2 needed to regenerate the acceptor. The major utility requirements are characterized by the power needed to overcome the reactor pressure drop and the steam required during regeneration and purging of the reactor. The flue gas flowrate is required to complete material balances and to determine the capacity of the reactor and thus the costs to treat a specific volume of gas. Finally, ammonia emissions are important since they can have potentially significant operational and economic impacts on equipment located downstream of an SCR system.

Two process measurements which are noticably absent from the list presented in Table 3-8 are the concentrations of NO_x and SO_2 at the inlet and outlet of the SFGT reactor. These measurements were not included in the audit program, but were subject to extensive examination in the continuous monitor certification tests.

The audit frequencies presented in Table 3-8 were selected based on several criteria. One consideration in specifying the audit frequencies was the availability/reliability of continuous process measurements. The most significant item which was not measured continuously on the pilot plant was the NH_3 concentration at the reactor outlet. As a consequence, the planned audit frequency for this measurement was relatively high.

Another consideration in determining the audit frequencies was the difficulty of making a particular measurement. If an audit is very time consuming this reduces the number of audits which can be conducted in a given period of time. An example of this is the H_2 flowrate at the SFGT pilot unit. It was expected that auditing the H_2 flowrate measurement would be difficult and so the frequency was lower.

It should be noted that the audit frequencies specified in Table 3-8 were initial frequencies and they changed as the QA program progressed. For the most part a change in audit frequency depended on the agreement between the audit result and the value of the process measurement recorded by UOP.

Figure 3-3 presents a decision chain which was used as a basis for changing the initial audit frequencies depending on the agreement between process measurements and the audit results. As shown, if the agreement was within ±5 percent, the audit frequency was decreased and the new frequency determined by the on site QA program leader. If the audit agreement was within ± 10 percent of the measured value, no change in frequency was made. If the audit agreement was outside the ± 10 percent range, corrective action was initiated to determine the source of error in either the audit procedure or the process measurement. At the same time, the audit frequency was increased. If the source of error was found and corrected, the audit frequency was reduced. However, if the error could not be resolved, the audit frequency was maintained at the maximum practical level within the time and manpower limits of the program. In addition to the use of relative accuracy of the QA audits as a basis for modifying the audit frequency, several practical considerations resulted in the reduction of the audit frequencies.

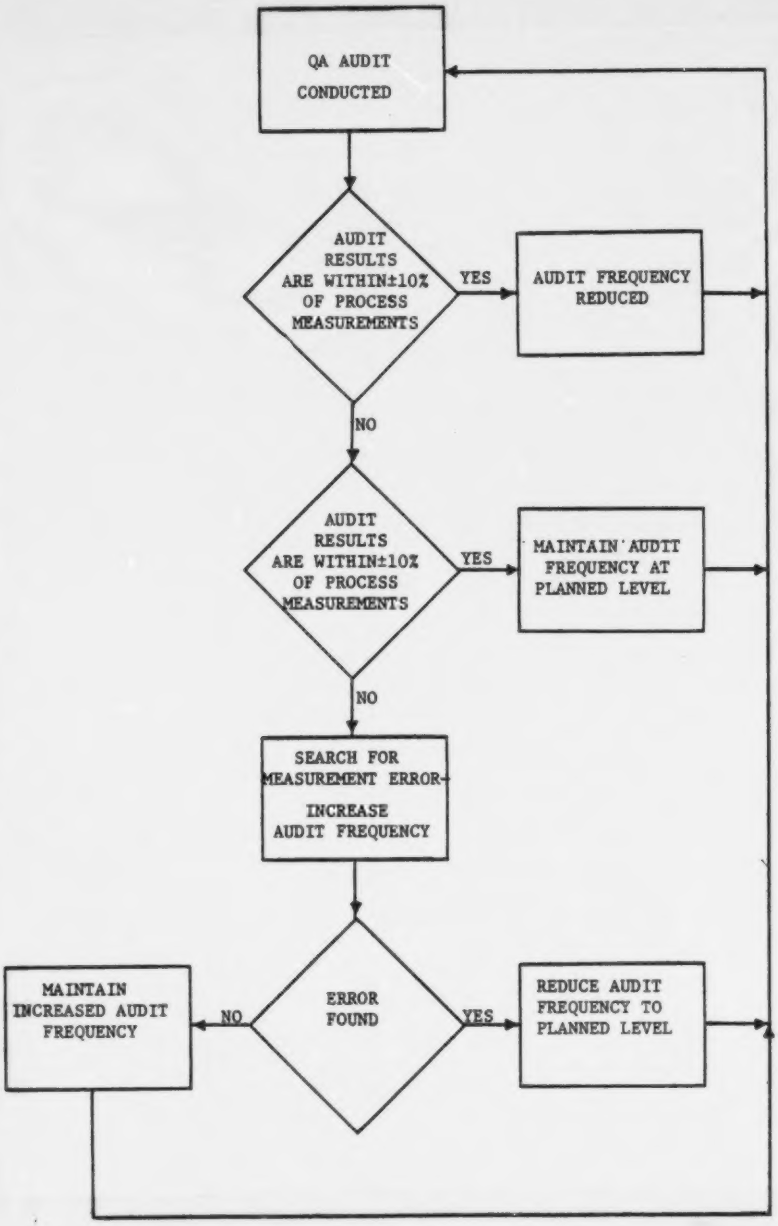
QA AUDIT CONDUCTED
AUDIT RESULTS ARE WITHIN±10% OF PROCESS MEASUREMENTS
YES
AUDIT FREQUENCY REDUCED
NO
AUDIT RESULTS ARE WITHIN±10% OF PROCESS MEASUREMENTS
YES
MAINTAIN AUDIT FREQUENCY AT PLANNED LEVEL
NO
SEARCH FOR MEASUREMENT ERROR-
INCREASE AUDIT FREQUENCY
ERROR FOUND
NO
MAINTAIN INCREASED AUDIT FREQUENCY
YES
REDUCE AUDIT FREQUENCY TO PLANNED LEVEL

Figure 3-3. Action plan based on QA audit results.

Table 3-8 presents the initial and actual audit frequencies for the QA audits. As shown, the actual audit frequencies are all lower than the planned frequencies. There are several reasons for this discrepancy. In the case of reactor pressure drop and flue gas inlet temperature, the agreement was excellent (±5 percent), and the frequency was reduced according to the decision chain shown in Figure 3-3. In the case of NH_3 injection rate, the agreement was good (±10 percent) and the difference was constant so no benefit was derived from a large number of audits. The audit frequencies for NH_3 emissions and flue gas flowrate were ultimately limited by access to the flue gas stream at the SFGT pilot plant. The sampling locations at the reactor inlet and outlet had to be shared between personnel conducting the QA audits and those conducting the stack sampling and continuous monitor certification tests. In the case of the H_2 and steam flowrates, it was impossible to conduct these audits without shutting down the pilot plant operation. As a consequence these process measurements were not audited. However, following the completion of the demonstration tests, the orifice plates used to measure H_2 and steam flowrates were calibrated by UOP personnel.

TABLE 3-8. INITIAL AND ACTUAL QUALITY ASSURANCE AUDIT FREQUENCIES AT SFGT PILOT UNIT

Process Measurement	Initial Audit Frequency (Audits/Week)	Actual Audit Frequency (Audits/Week)
Flue Gas Flowrate	3	2.5
NH_3 Injection Rate	3	1
Reactor Pressure Drop	3	2
Reactor Inlet Temperature	3	2
NH_3 Emissions	10	3
H_2 Flowrate	0.5	0
Steam Flowrate	0.5	0

Detailed results of the QA audits are presented in Appendix A while a summary and discussion of the audit results are presented in Section 4.

3.4.2 Secondary Emissions Sampling

Secondary emissions sampling was included as an element of the independent evaluation test program to quantify changes in the emission rates of selected secondary pollutants (pollutants other than NO_x or SO_2) which resulted from processing flue gas in the SFGT reactor. The emphasis on secondary pollutants was primarily environmental and the sampling program was designed to determine if the reduction in NO_x/SO_2 emissions by the SFGT process produced an increase in some other, potentially more harmful pollutant. However, in some cases, it was anticipated that the SFGT process might actually reduce the emission rates of pollutants other than NO_x and SO_2 and the secondary emissions sampling was also designed to quantify this.

Pollutants of Interest

Table 3-9 presents the secondary emissions sampling plan which identifies the pollutants to be measured, the sampling locations, and the number of samples to be collected at each location. The pollutants included in Table 3-9 were selected based on available information about SCR processes and on concerns expressed by the professional community. The following discussion briefly examines the reasons for measuring each of the pollutants shown in Table 3-9.

Sulfur Trioxide (SO_3)--

Sulfur trioxide was measured at the inlet and outlet of the SFGT pilot plant reactor to determine if any change in concentration occurs since. UOP had indicated that the SFGT acceptor may remove SO_3 from the flue gas (see Equation 3-6). This represents a beneficial aspect of the process which can result in an improvement in boiler efficiency through reduction of the acid dewpoint.

TABLE 3-9. SECONDARY EMISSIONS SAMPLING PLAN

Pollutant Measured	Sampling Location	Number of Samples at each Location
Sulfur Trioxide (SO_3)	Reactor Inlet/Outlet	6
Particulate Concentration	Reactor Inlet/Outlet	3
Particulate Composition	Reactor Inlet/Outlet	3
Carbon Monoxide (CO)	Reactor Inlet/Outlet	3
Hydrocarbons (C_1-C_6)	Reactor Inlet/Outlet	3
Hydrogen Cyanide (HCN)	Reactor Inlet/Outlet	3
Nitrosoamines	Reactor Inlet/Outlet	3
Nitrous Oxide (N_2O)	Reactor Inlet/Outlet	3

Particulate Concentration and Composition--

Particulate samples were collected and analyzed at the SFGT pilot plant. Particulate concentration in the flue gas was measured to document the concentration the reactor was exposed to and thus demonstrate the ability of the reactor to operate under high particulate loadings. Particulate composition was measured to determine if catalyst erosion in the reactor had a measurable effect on the concentration of trace elements in the particulates. This was done by examining particulate composition at the reactor inlet and outlet and determining if any increase in the concentration of the elements present in the catalyst (copper and aluminum) occurred.

Carbon Monoxide (CO) and Hydrocarbons (HC)--

Carbon monoxide and hydrocarbons were measured at the reactor inlet and outlet to determine if any change occurs in the concentration of these pollutants across the reactor. These two pollutants are of interest since they can both be oxidized by oxygen or NO_x. As a consequence, it is possible that in addition to NO_x and SO_2, the reactor may also reduce the emission levels of CO and/or HC.

Hydrogen Cyanide (HCN), Nitrosoamines, and Nitrous Oxide (N_2O)--

Hydrogen cyanide, nitrosoamines and nitrous oxide were measured to determine if any change in the concentration of these compounds occurred in the SFGT reactor. While no concrete evidence exists to indicate that HCN, nitrosoamines, or N_2O are produced, concern has been expressed that the presence of NH_3 and the catalyst may result in production of one or more of these compounds. The sampling program was designed to measure each of these compounds and document any change in their concentrations across the reactor.

Sampling Strategy

Because the SFGT pilot plant operated as a cyclic process, reactor operating conditions and flue gas exit composition changed continuously during the course of an acceptance period. As a result, it was necessary to carefully schedule the sampling periods so meaningful data could be obtained. In the case of SO_3, HCN, and nitrosoamines, this involved sampling at a constant rate over the entire acceptance period. This integrated sampling technique was designed to give an average concentration during an acceptance period. In the case of particulate sampling, the particulate concentration in the flue gas was not affected by the cyclic nature of the process. Therefore, sampling was conducted when convenient. Because the sampling techniques for hydrocarbons, CO, and N_2O required the collection of "grab" samples, it was not possible to obtain a sample which was integrated over the entire acceptance period. As a result, samples of these species were collected when changes in the concentrations of NO_x and SO_2 in the reactor effluent were gradual (see Figure 3-1).

Analysis of all but the nitrosoamine samples were completed on site during the secondary emissions tests. On-site analysis was provided to give timely feed back in the event anomalous results were obtained. Details of both the sampling and analysis procedures along with sampling results are presented in Appendix B. Results of the secondary emissions sampling tests are also summarized in Section 4.

3.4.3 Continuous SO_2 and NO_x Monitor Certification

The final element of the independent evaluation test program involved the certification of the continuous monitors which measured reactor inlet and outlet concentrations of NO_x and SO_2. Certification of continuous emission monitors involves a formal procedure which has been developed by EPA to insure the accuracy of monitors measuring emissions from sources which must comply with new source performance standard emission limitations. In order for a continuous emission monitor (CEM) to be certified, it must be subjected to and pass a number of performance tests. These tests include:

- Calibration Error,
- Response Time,
- 2- and 24-hour Zero Drift,
- 2- and 24-hour Calibration Drift, and
- Relative Accuracy.

The performance specifications for each of the above certification tests are shown in Table 3-10. These specifications are those contained in the Federal Register, Vol. 44, No. 197, Wednesday, October 10, 1979 - "Proposed Rules: Standards of Performance for New Stationary Sources; Continuous Monitoring Performance Specifications".[3]

The following discussion briefly describes each certification test, identifies areas where the certification tests at the SFGT pilot plant differed from those outlined in the performance specifications, and presents reasons for the differences. A summary of the certification results is presented in Section 4 with detailed results in Appendix C. For more details of the certification test procedures, the reader is referred to the Federal Register mentioned above.

TABLE 3-10. CONTINUOUS MONITORING SYSTEM PERFORMANCE AND EQUIPMENT SPECIFICATIONS

Certification Test	Performance Specification
Calibration Error	≤ 5 percent for mid-range and high level calibration gases
Response Time	≤ 15 minutes
Zero Drift (2-hour)	≤ 2 percent of Span[1] value
Zero Drift (24-hour)	≤ 2.5 percent of Span[1] value
Calibration Drift (2-hour)	≤ 2 percent of Span[1] value
Calibration Drift (24-hour)	≤ 2.5 percent of Span[1] value
Relative Accuracy	≤ 20 percent of reference method test data in terms of emission standard[2] or 10 percent of the applicable standard, whichever is greater

[1] Span refers to the range of the emission monitor (e.g., 0-500 ppm).
[2] Emission standards are expressed in terms of pollutant mass emissions per unit of heat input.

Calibration Error

Calibration error is a measure of the ability of a continuous monitor to accurately analyze the concentration of a calibration gas. To determine calibration error, a series of 15 measurements are made; 5 each of high and mid-level calibration gas concentrations and 5 of zero gas (air). The measurements are made such that the same gas concentration is not measured two or more times in a row (i.e., non-consecutively). The calibration error is then determined by the difference between the concentration of the calibration gas (which has been verified by one of several techniques defined in the CEM performance specifications) and the continuous monitor readings. Specifically the error is defined by Equation 3-8.

$$\text{Calibration Error} = \frac{|\bar{X}| + |CI_{95}|}{RV} \qquad (3\text{-}8)$$

where $|\bar{X}|$ = absolute value of the mean difference between the monitor reading and the calibration gas concentration.

RV = concentration of the calibration gas.

$|CI_{95}|$ = absolute value of the 95 percent confidence interval which is defined by Equation 3-9.

$$CI_{95} = \frac{t_{.975}}{n(n-1)^{1/2}} \left(n\sum X_i - \left(\sum X_i\right)^2\right)^{1/2} \qquad (3\text{-}9)$$

where n = the number of measurements (in this case 5)

$t_{.975}$ = 2.776 (for 5 measurements)

X_i = difference between the continuous monitor reading and the calibration gas concentration for individual readings.

For the continuous monitor to pass the calibration error test, the error as defined by Equation 3-8 must be less than or equal to 5 percent for both the mid- and high-range calibration gases. There was no deviation from this procedure in conducting the calibration error test at the SFGT pilot plant.

Response Time

Response time is a measure of the time which elapses before a continuous monitor responds to a change in the pollutant concentration in a duct. To determine response time, zero gas is introduced into the continuous monitor's sampling system at the duct/sample line interface. Once the monitor reading stabilizes at zero, the sampling system is switched from zero gas to monitoring the stack effluent and the time required for the monitor to reach a stable reading is determined. This is the upscale response time. Subsequently, the downscale response time is determined by introducing high-level calibration gas into the continuous monitor sampling system at the duct/sample line interface. Once the monitor's reading stabilizes at the high level gas concentration, stack gas is introduced into the sample line and the time required for the monitor's reading to reach a stable value downscale is determined. This procedure is repeated three times and the mean upscale and downscale response times are determined. The maximum of these values must be less than 15 minutes for the continuous monitor to pass this test.

At the SFGT pilot plant it was not possible to measure response time according to the procedure defined above without causing loss of data and a possible loss of a compliance day during the demonstration. Instead, response time was determined during the regeneration period (when no flue gas was flowing through the reactor) by alternately introducing zero and high-level calibration gas into the sample line at the duct/sample line interface. Upscale response time was that required to stabilize the CEM system reading after the switch from air to the high-level calibration gas while downscale response time was measured in the opposite manner.

Zero and Calibration Drift

Zero and calibration drift are measures of how the continuous monitor's response to zero and calibration gases changes with time. To measure two-hour drift, zero and high level calibration gases are introduced into the instrument at two-hour intervals. The differences between the monitor readings and the zero or calibration gas concentrations are recorded until 15 sets of data are obtained. Drift is then calculated using Equations 3-8 and 3-9 where the reference value (RV) equals the range of the continuous monitor and $t_{.975}=2.145$ (for 15 tests). 24-hour drift is measured in a similar manner. At the start of a 24-hour period the monitor is calibrated and zeroed and then no further adjustments are made. After 24 hours, zero and calibration drift are recorded and the instrument is recalibrated. A total of 7 measurements are required to determine 24-hour drift and Equations 3-8 and 3-9 are used. For 7 measurements, $t_{.975}=2.447$.

Because the SFGT pilot plant was an experimental system, the accuracy continuous monitors was of particular concern. As a consequence, the calibration and zero settings on the continuous monitors were adjusted about once per hour (generally at the start and completion of an acceptance period). Obviously, the 24-hour drift test is not meaningful under these circumstances and the two-hour drift test could not be completed strictly according to performance specifications. Instead, the zero and calibration drift was determined over an acceptance period between initial and final calibration and zeroing of a monitor.

Relative Accuracy

Relative accuracy is the most important test in determining the performance of the continuous monitors. This test is comparison of a continuous monitor's analysis of stack gas with a stack gas analysis as determined by EPA reference methods (Method 3 for O_2 and CO_2, Method 6 for SO_2, and Method 7 for NO_x). Relative accuracy is determined by making a minimum of 9 reference method tests (for Method 7, one test requires three samples) and comparing the results to the continuous monitor readings during the time the reference tests were collected. In addition, for determining the relative accuracy of NO_x and SO_2 continuous monitors, simultaneous reference method tests for O_2 or CO_2 are required so the NO_x and SO_2 concentrations can be converted to a mass emissions per unit of heat input (e.g., $lb/10^6$ Btu) basis.

After the reference method tests are completed and the continuous monitor and reference method test results are converted from concentrations to a mass emission per unit heat input basis, the relative accuracy can be determined. Relative accuracy is calculated using Equations 3-8 and 3-9 where the reference value (RV) is equal to the mean of the reference method tests and $t_{.975}$=2.306 (for 9 tests)

9 sets of reference method tests for both SO_2 and NO_x were completed at the inlet and outlet of the SFGT pilot plant reactor. However, reference method tests for O_2 or CO_2 were not included because UOP did not operate an O_2 or CO_2 monitor. As a result, the CEM data could not be converted to a mass

emission per unit of heat input basis. In the case of the SFGT pilot plant this does not impact the validity of the relative accuracy tests because (1) the reactor operated under 7.5 kPa (30 in H_2O) pressure so no dilution occurred between the reactor inlet and outlet, and (2) the measurements made by the continuous monitors were intended to demonstrate the ability of the process to achieve a specific percentage reduction in NO_x and SO_2 emissions based on pollutant concentrations rather than a reduction in emissions below a specific mass emission rate per unit heat input.

SECTION 4

SFGT PILOT PLANT TEST RESULTS

The SFGT pilot plant tests conducted by both UOP and Radian were designed to establish the technical and economic feasibility of the SFGT process. The results of the two test programs can be combined and used to complete energy and material balance calculations and to size an SFGT reactor for a specific application. This section presents a summary and discussion of the most significant results of the two test programs. The information presented here serves as a basis for the technical evaluation presented in Section 5 and the R & D requirements defined in Section 6. For a more detailed presentation of UOP's test results, the reader is referred to UOP's final report on this pilot plant test program, while additional details of Radian's test results are contained in the appendices to this report.

As discussed earlier, the UOP tests were divided into two phases, optimization tests and demonstration tests. And Radian's program consisted of three elements: Quality assurance audits, secondary emissions sampling, and continuous monitor certification. The results of these tests are presented individually in this section but the accompanying discussion examines the impact of each group of tests on the overall process and process evaluation.

4.1 OPTIMIZATION TESTS

The optimization tests conducted by UOP were initially intended to identify operating conditions which resulted in 90 percent reduction in both NO_x and SO_2 emission rates while minimizing costs. However, after the test program was initiated, the objective of the optimization tests was modified.

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The new objective was simply to identify operating conditions which would result in 90 percent reduction in both NO_x and SO_2 emissions. This objective was met during the final weeks of the test program using the UOP acceptor.

Between the initiation of the SFGT pilot plant test program in October 1979 and its conclusion in 1980, a large number of optimization tests were conducted. This section summarizes some of the most significant test results. It also examines the implication of the test results on application of the SFGT process to a commercial system. It should be noted that not all test results are presented here. For more details of both tests and results the reader is referred to UOP's report on the test program.

4.1.1 Effect of Flue Gas/Reactor Inlet Temperature on Pilot Plant Performance

As discussed earlier, flue gas/reactor inlet temperature can impact both NO_x and SO_2 reduction efficiencies. During the optimization tests the influence of flue gas temperature was examined while the pilot plant was operated for SO_2 removal only, NO_x reduction only, and both NO_x and SO_2 reduction. The following discussion examines the effect of temperature on the SO_2 removal and NO_x reduction efficiencies of the pilot plant.

SO_2 Removal

Prior to the test program it was anticipated that an increase in flue gas temperature would increase the SO_2 removal efficiency of the SFGT process. This expectation was confirmed by the results of the optimization tests as shown in Table 4-1. The data presented in Table 4-1 show a small but consistent increase in the SO_2 removal efficiency with an increase in temperature. These data represent averages of several cycles and they were selected such that other variables which can influence SO_2 removal efficiency remained relatively constant at both temperature levels. All the data shown are from tests on the second acceptor.

TABLE 4-1. EFFECT OF FLUE GAS/REACTOR INLET TEMPERATURE ON SO_2 REMOVAL EFFICIENCY

Cycle	Inlet Temp. (°C)	SO_2 Removal (%)	Flowrate (Nm^3/hr)	Inlet SO_2 Concentration (ppm)	Acceptance Time (Min)	Process Gas
312-316	402	75.0	1600	2360	99	Air
321-325	426	76.8	1630	2390	99	Air
419-421	402	88.8	1560	2170	70	Air
397-413	427	90.5	1630	2140	70	Air
430-433	399	84.1	1630	2140	70	Flue Gas
449-487	424	85.4	1610	2110	70	Flue Gas

The relatively small increase in SO_2 removal efficiency as a function of temperature indicates that the rate of the chemical reaction between SO_2 and CuO may not be the step which limits SO_2 removal efficiency from a gas stream. Typically, changes in temperature produce large changes in the chemical reaction rate. The rate of mass transfer, on the other hand, is relatively insensitive to temperature.

Since mass transfer may control the rate of the SO_2 removal reaction in the temperature range from 400 to 425°C, some useful conclusions can be drawn from the test results. First, the apparent effect of temperature on SO_2 removal should not be extrapolated to lower temperatures. Because chemical reaction rate can be more sensitive to temperature than the rate of mass transfer, the effect of temperature on SO_2 removal could be significantly different at lower temperatures, thus making extrapolation of the pilot plant test results inaccurate.

Second, some control of temperature may be required at the reactor inlet if an SFGT process is installed to meet NSPS which require 90 percent reductio in SO_2 emissions. If the flue gas temperature at the economizer exit drops, the removal would drop below design levels and result in violation of emission standards. This could occur as a result of a change in boiler load in which the flue gas temperature can change by as much as 100°C. To some extent the drop in load would be offset by lower flue gas flowrates. But, since reactor performance at lower temperatures cannot be determined from the pilot plant test data, a conservative design requires the use of temperature control to insure the SFGT system would meet the emission standard. This design could be modified if the SO_2 removal is characterized at lower temperatures.

NO_x Removal

Prior to the start of the optimization tests it was anticipated that an increase in reactor inlet temperature would result in an increase in NO_x reduction. Then at some temperature, increased NO_x reduction would be offset by increased NH_3 oxidation. The results of the tests which examined the effects of temperature on NO_x reduction are presented in Table 4-2. The data in this table are based on averages and were selected so operating parameters which can affect NO_x reduction efficiency were relatively constant at varying reactor inlet temperatures.

TABLE 4-2. EFFECT OF TEMPERATURE CHANGES ON NO_x REDUCTION DURING NO_x/SO_2 AND NO_x ONLY TESTS

Test Type	Inlet Temp. (°C)	NO_x Reduction (%)	Flowrate (Nm^3/hr)	NH_3/NO_x Injection Ratio	Acceptance Time (min)	Process Gas
NO_x/SO_2 (cycle)						
365-369	400	86.7	1580	1.59	70	Air
373-381	425	79.8	1580	1.60	70	Air
414-418	412	85.6	1610	1.70	70	Air
406-413	427	80.4	1580	1.77	70	Air
NO_x-only (date)						
7/9	404	85.8	1610	1.19	-	Flue Gas
7/10	416	84.6	1600	1.19	-	Flue Gas
10/15-	400	80.7	1610	.99	-	Flue Gas
10/16	416	86.2	1600	1.00	-	Flue Gas
10/17-	415	93.8	1600	1.22	-	Flue Gas
10/18	430	94.1	1600	1.20	-	Flue Gas

The data in Table 4-3 indicate that the time averaged NO_x reduction efficiency decreased with increasing temperature during cyclic operation. One possible explanation for this behavior is that during cyclic operation, an increase in temperature increases NH_3 oxidation at the start of the acceptance period. As the regenerated acceptor is oxidized to CuO, heat generated by this reaction causes the temperature of the acceptor and reactor internals to rise to approximately 500°C. At this temperature, NH_3 oxidation becomes significant. As flue gas passes through the reactor, the acceptor is cooled and NH_3 oxidation decreases. The effect of increasing the temperature of the flue gas entering the reactor would be to decrease the rate at which the acceptor and reactor internals are cooled, thus increasing the quantity of NH_3 oxidized during an acceptance period. This explanation is supported by the results of the preoxidation tests which indicate that the temperature of the reactor internals at the start of an acceptance period has a significant impact on NO_x reduction efficiency (see Section 4.1.7).

The tests during NO_x only operation should show the effect of temperature on instantaneous NO_x reduction efficiency. However, based on the data in Table 4-3, it is not clear what the effect temperature is. In the first case, increased inlet temperatures produce a slight decrease in NO_x reduction efficiency, in the second case, a significant increase, and in the third case, NO_x reduction efficiency is essentially unchanged. Because of these conflicting results, no conclusion can be drawn concerning the effect of temperature on instantaneous NO_x reduction.

In terms of applying the SFGT process for simultaneous reduction of NO_x and SO_2 emissions, the results from the NO_x/SO_2 only tests may be more applicable although this depends on how the process is operated. If acceptance is initiated with a regenerated reactor containing elemental copper, an increase in flue gas temperature would be expected to decrease the time averaged NO_x removal efficiency. The exact relationship between temperature and NO_x reduction would depend on the reactor design.

Summary

Assuming the reactor design and operation employed in the pilot plant tests is applied to a commercial SFGT system, it will be necessary to minimize fluctuations in the temperature of the flue gas entering the reactor above or below the design temperature. If the flue gas temperature drops below design temperature, time averaged SO_2 removal will decline and if flue gas temperature increases above the design temperature, time averaged NO_x removal will decrease.

4.1.2 The Effect of Flue Gas Flowrate on Pilot Plant Performance

Changes in flue gas flowrate can impact both NO_x reduction and SO_2 removal in an SFGT reactor, depending on the system design and type of operation. The discussion presented here will focus on the effects of flowrate changes on cyclic operation. Flowrate effects on SO_2 removal and NO_x reduction will be examined separately although the impacts are interrelated.

SO_2 Removal

The nature of the SFGT process is such that, for a given reactor design, nearly any time-averaged SO_2 removal efficiency can be attained by varying the length of the acceptance period. But since the parallel passage reactor contains a fixed quantity of acceptor material, it has a limited capacity for SO_2 removal. Any change in the quantity of SO_2 entering the reactor will result in a change in the time averaged SO_2 removal efficiency for a fixed acceptance period.

Figure 4-1 presents the results of tests in which the quantity of SO_2 entering the pilot plant reactor was varied, primarily by varying flowrate. During these tests, acceptance time was fixed and other operating parameters remained relatively constant. As shown, the time averaged SO_2 removal efficiency decreased significantly as the flowrate was increased.

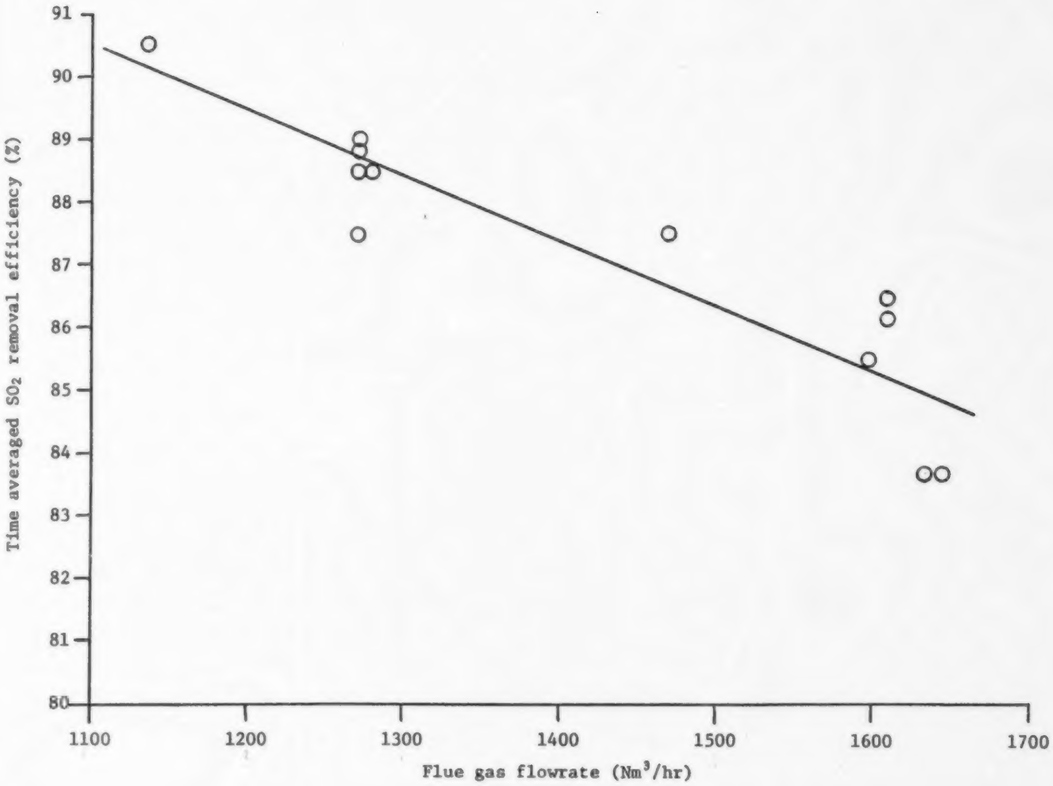

Figure 4-1. The effect of flue gas flowrate on the time averaged SO_2 removal efficiency of the SFGT pilot plant.

The decrease in SO_2 removal efficiency was due to the increased quantity of sulfur dioxide entering the reactor and not due to a change in the SO_2 reaction rate. In fact, the SO_2 reaction rate actually increased with increasing flowrate. This is illustrated in Figure 4-2 which shows the rate of SO_2 removal from the flue gas as a function of flowrate. The data in Figure 4-2 indicate that the SO_2 reaction rate increased by 30 percent as flowrate was increased from 1200 to 1600 Nm^3/hr. This increase could be the result of several changes which occur as flowrate is increased. Because removal decreased as flowrate increased, the time averaged SO_2 concentration in the reactor also increases. Since the SO_2 removal reaction appears to be first order with respect to SO_2 concentration, the reaction rate would increase in proportion to the increase in time averaged SO_2 concentration.

As evident from Figure 4-1, the change in time averaged SO_2 concentration is too small to account for the large change in reaction rate. A second change which occurs at increased flowrates is an increase in turbulence in the reactor. This would tend to improve mass transfer from the bulk gas to the surface of the catalyst. It appears that this effect is largely responsible for the increase in SO_2 reaction rate with increased flowrates. This indicates that the acceptor would be used more effectively at higher flowrates.

NO_x Reduction

Several sets of tests were conducted which examined the effect of flowrate on NO_x reduction efficiency. Some results from these tests are presented in Figure 4-3. These data are from tests during both cyclic and NO_x only operation and were selected so all other operating parameters were relatively constant at both flowrates. As shown, changes in flowrate have essentially no effect on NO_x reduction efficiency. This indicates that, over the range of flowrates tested the rate of the NO_x reduction reactions increased in direct proportion to the flowrate.

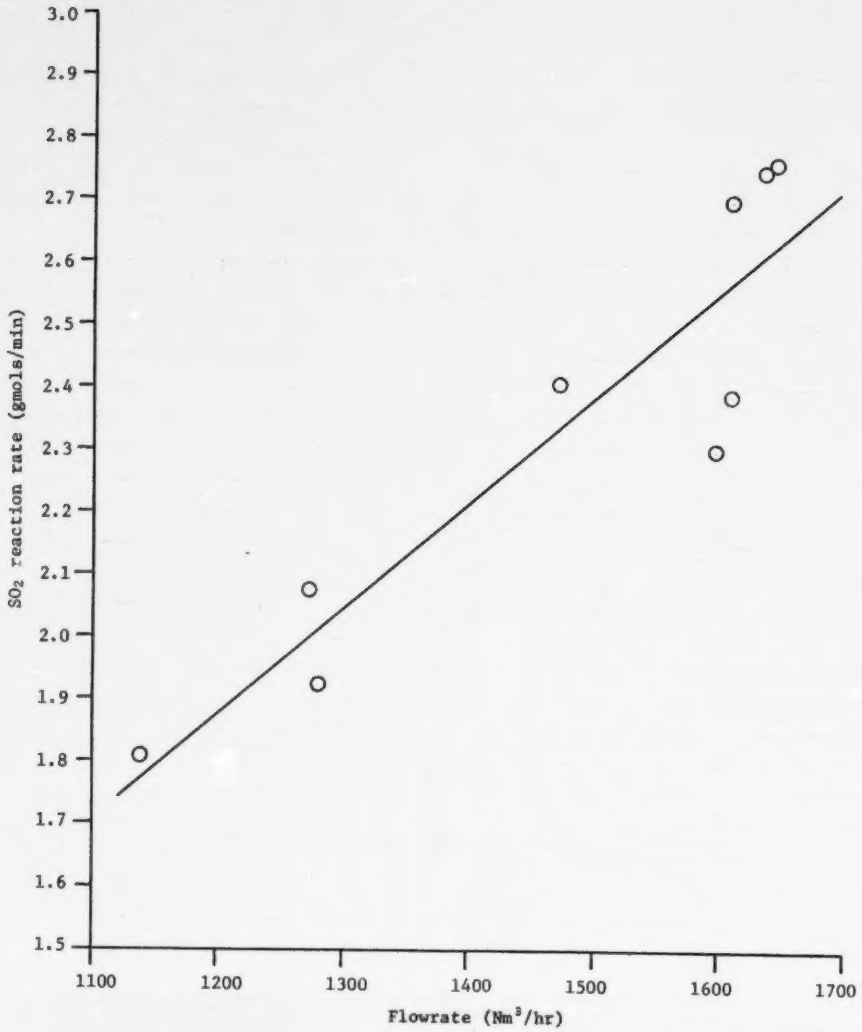

Figure 4-2. SO_2 reaction rate as a function of flue gas flowrate.

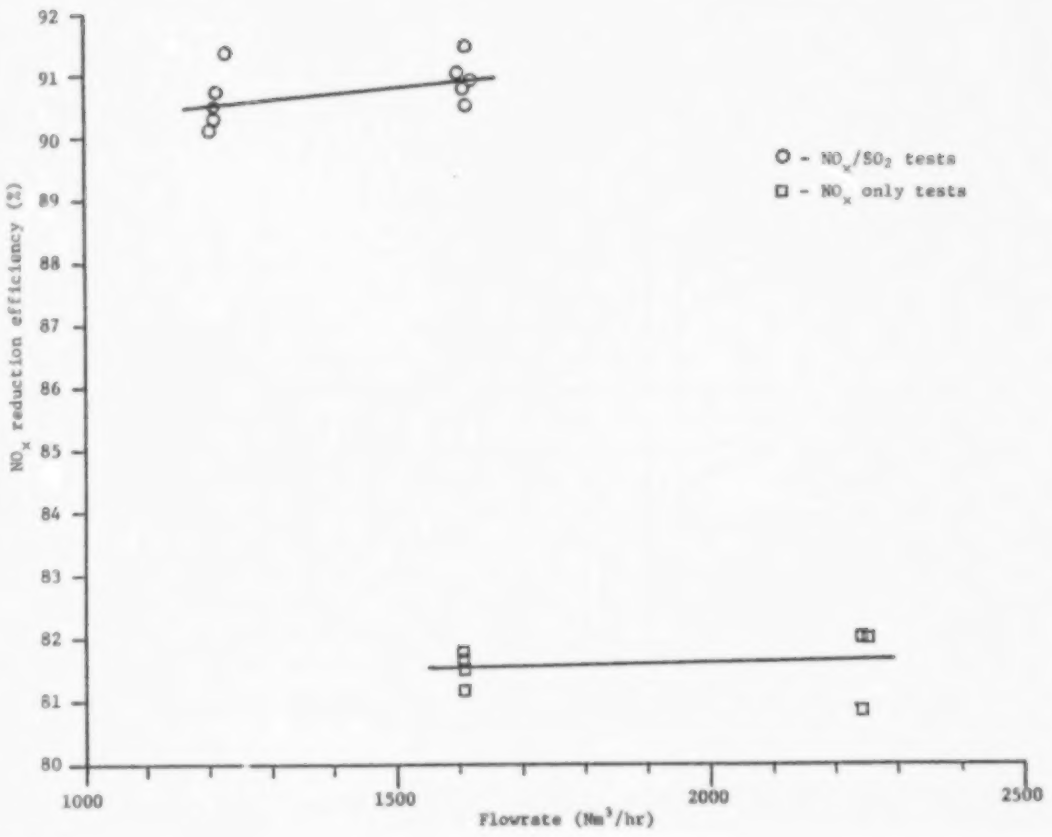

Figure 4-3. NO_x reduction as a function of flue gas flowrate.

Figure 4-4 illustrates the relationship between flowrate and the rate of the NO_x reduction reactions. As shown, an increase in flowrate produces a 1 to 1 increase in the reaction rate. Since no change occurs in the time averaged NO_x concentration in the reactor, the increase in reaction rate is due to increased turbulence. As with SO_2, this indicates that more effective use of the acceptor will result at higher flowrates.

Summary

The effects of flowrate on NO_x reduction and SO_2 removal in the pilot plant indicate that a commercial design should maximize flowrate to maximize acceptor utilization. However, the benefit of increased flowrates and consequent increased NO_x and SO_2 reaction rates must be weighed against the cost of increased reactor pressure drop. UOP has identified the optimum flowrate for the parallel passage reactor design as approximately 1600 Nm^3/hr per unit cell (0.25 m^2 in crossection) at 400°C.

A commercial design of an SFGT process should be for the maximum flowrate expected. At flowrates below design, time averaged SO_2 removal will improve (or acceptance time can be extended) while NO_x reduction will be unaffected. At reactor feedrates above the design level NO_x reduction efficiency should not be affected, but the time averaged SO_2 removal efficiency will decline. In this situation, design SO_2 removal efficiency could be maintained by reducing the acceptance time but then NO_x reduction efficiency would decline. In either event, it would not be possible to maintain both SO_2 removal and NO_x reduction at design levels if the reactor feedrate increased above its design level.

4.1.3 The Effect of Acceptance Time on Pilot Plant Performance

The length of an acceptance period can impact both NO_x reduction and SO_2 removal efficiencies of the SFGT process. For a fixed reactor design and constant operating conditions, an increase in acceptance time results in an increase in time averaged NO_x reduction and a decrease in time averaged SO_2

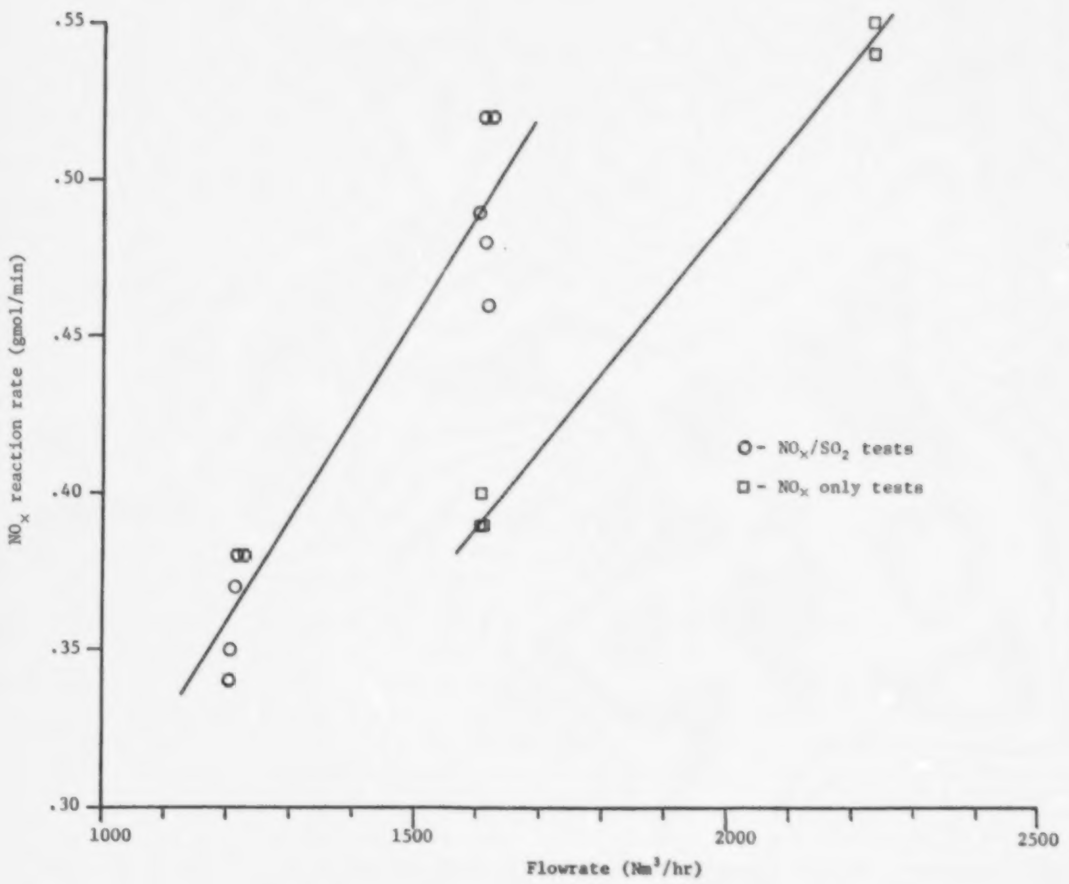

Figure 4-4. NO_x reaction rate as a function of flue gas flowrate.

removal. Some of the factors which produce these changes are the same while some factors may influence either NO_x reduction or SO_2 removal independently. The following discussion examines the observed effects of acceptance time on SO_2 removal and NO_x reduction efficiencies.

SO_2 Removal

Figure 4-5 is a typical example of how instantaneous SO_2 removal changed as a function of acceptance time during tests with the second acceptor. As shown, after an initial peak, the instantaneous SO_2 removal efficiency decreases continuously as the acceptance time increases. The peak in this curve corresponds to the point at which all elemental copper has been oxidized and the quantity of CuO in the reactor is at a maximum. The subsequent decline in removal efficiency over the remainder of the acceptance period is primarily due to the fact that the quantity of CuO in the reactor decreases as SO_2 is removed and $CuSO_4$ is produced. Assuming all other operating variables remain constant, the relationship between instantaneous SO_2 removal and the quantity of CuO in the reactor can be determined.

In addition to reducing the quantity of CuO available for reaction, $CuSO_4$ formation may also reduce the instantaneous SO_2 removal rate by decreasing the pore volume of the catalyst pellets. The molar volume of $CuSO_4$ is about 3.5 times that of copper oxide. Therefore, as $CuSO_4$ is formed, it could tend to restrict diffusion within the catalyst pores and thus reduce the instantaneous SO_2 removal efficiency.

NO_x Reduction

Figure 4-6 is a typical example of how instantaneous NO_x reduction changed as a function of acceptance time during tests with the second acceptor. As shown, the initial NO_x reduction efficiency was very poor (in fact it was negative during the first few minutes of acceptance due to NH_3 oxidation). The NO_x reduction efficiency then improved during the acceptance period until a steady state level was reached. At this point, instantaneous NO_x reduction

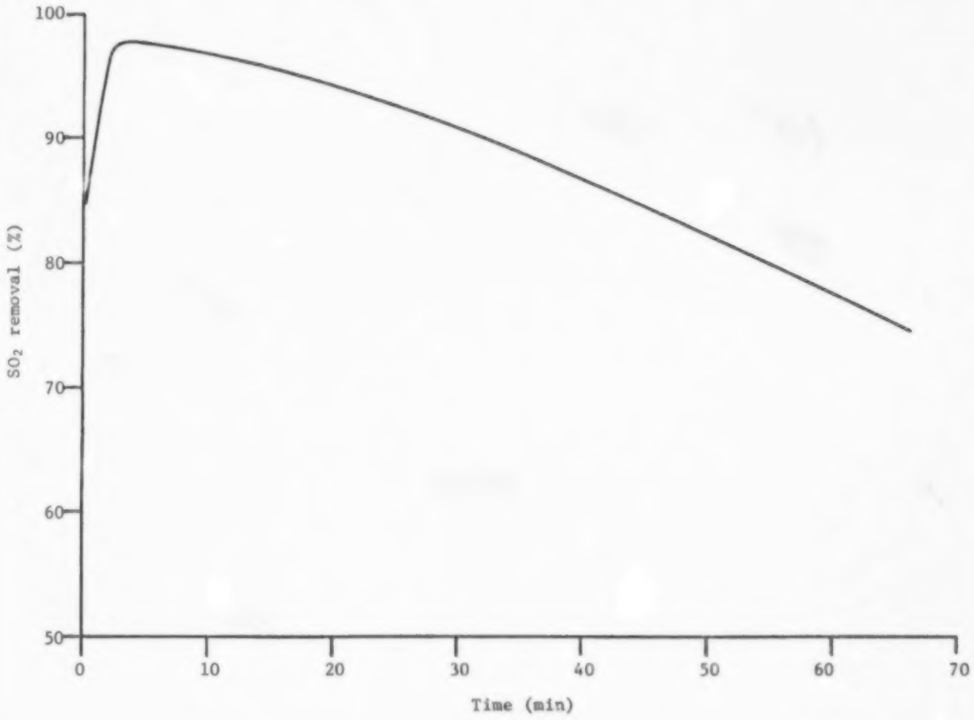

Figure 4-5. Typical SO$_2$ removal vs time curve for the SFGT pilot plant.

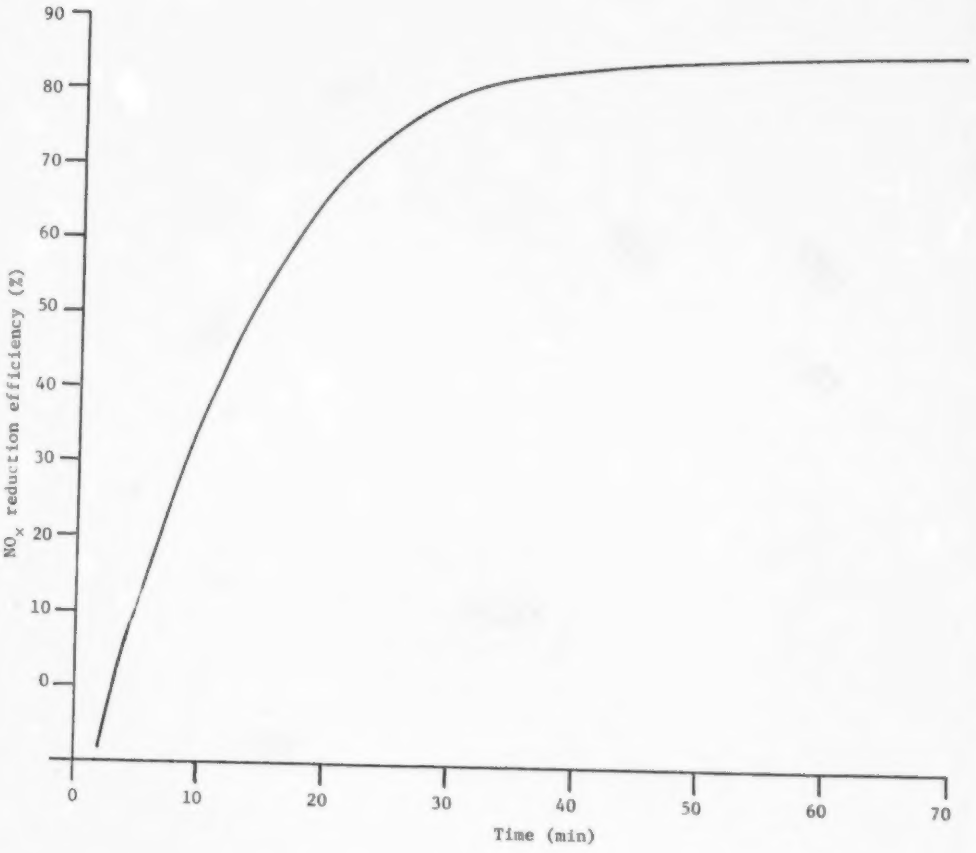

Figure 4-6. Typical NO_x reduction vs time curve for the SFGT pilot plant.

efficiency was relatively constant for the remainder of the acceptance period while the time averaged NO_x reduction efficiency continued to increase. This is a result of averaging the poor NO_x reduction at the start acceptance over a longer period of time.

It appears that at least two factors influence the time averaged NO_x reduction efficiency over the duration of an acceptance period. During the first part of acceptance the instantaneous NO_x reduction is poor. This is due to high temperatures in the reactor which cause NH_3 oxidation and thus lower the NO_x reduction efficiency. As the reactor begins to cool, NO_x reduction efficiency improves. Once the reactor internals have cooled NO_x reduction efficiency reaches a steady state level. At this point, the temperature in the reactor no longer limits the reaction rate. Instead, it appears that the NH_3/NO_x injection ratio determines the steady state NO_x reduction efficiency.

Summary

It is evident from the preceeding discussion that the NO_x reduction efficiency and SO_2 reduction efficiency of the SFGT process are interrelated. A change in acceptance time produces opposite changes in NO_x reduction and SO_2 removal efficiencies and so it would seem to be difficult to use acceptance time as a design variable. However, changes can be made in other process operating parameters while varying acceptance time and desired NO_x and SO_2 reduction efficiencies achieved. For example, if the acceptance time is too short to achieve a specific time averaged NO_x reduction efficiency, it can be extended and NO_x reduction efficiency improved. At the same time, SO_2 removal efficiency can be maintained at a constant level by adding additional acceptor to the reactor.

In designing a commercial scale SFGT process, it is necessary to insure the acceptance time is long enough to attain the desired NO_x reduction efficiency and to permit adequate time for regeneration of the acceptor while still maintaining SO_2 removal efficiency at design levels. Therefore, any commercial design should use the maximum possible SO_2 concentration as basis. If the SO_2 concentration entering a reactor increases above the design level, acceptance time would have to be reduced to maintain SO_2 removal at the design level. Assuming other operating parameters are constant, this would result in a decrease in NO_x reduction below design levels. If the acceptance time is not reduced, the SO_2 removal efficiency would fall below design levels.

4.1.4 The Effects of NH_3/NO_x Injection Ratio on Pilot Plant Performance

Changes in the NH_3/NO_x injection ratio can affect both the steady state and time averaged NO_x reduction efficiency of the SFGT process. However, changes in this ratio do not appear to affect the SO_2 removal efficiency. During the optimization tests, an attempt was made to quantify the impact of changes in NH_3/NO_x injection ratio on the time averaged and steady state NO_x reduction. In the case of NO_x reduction during cyclic operation, quantative results were not obtained although the expected result of increased NO_x reduction at increased NH_3/NO_x injection ratios was confirmed. The effects of the NH_3/NO_x injection ratios could not be quantified because changes in other process operating parameters also affected NO_x reduction.

Tests were conducted which successfully quantified the effect of changes in the NH_3/NO_x injection ratio on steady state NO_x reduction efficiency. These tests were completed during "NO_x only" operation in which the copper in the acceptor was all in the form of $CuSO_4$. Since the quantity of $CuSO_4$ remained constant, the effects of changes in the NH_3/NO_x injection ratio on NO_x reduction could be easily isolated. The results of these tests are presented in Figure 4-7. In addition, Figure 4-7 shows NH_3 emissions from the reactor as a function of the NH_3/NO_x injection ratio. The NH_3 emission levels were determined by stack sampling tests conducted by UOP and the results are consistent with the results of tests conducted by Radian.

The relationships shown in Figure 4-7 illustrate the trade-off between improved NO_x removal efficiencies and increased NH_3 emissions. At NH_3/NO_x injection ratios below 1.0, increases in the NH_3/NO_x injection ratio produce

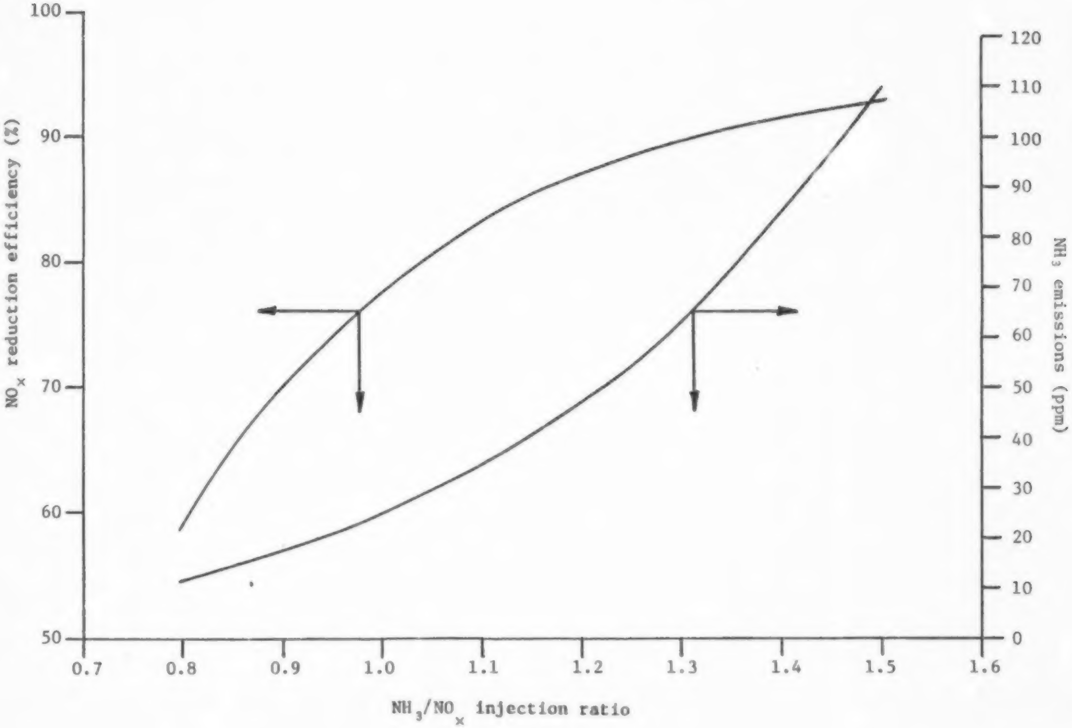

Figure 4-7. NH_3 emissions and NO_x reduction efficiency as a function of NH_3/NO_x ratio

relatively large improvements in NO_x reduction efficiency with relatively small increases in NH_3 emissions. However, as the NH_3/NO_x injection ratio is increased above 1.0, the rate of increase in NO_x reduction decreases while NH_3 emissions increase at a more rapid rate. These data can be used to evaluate the trade-off between improved NO_x reduction and increased NH_3 emissions. However, the steady state NH_3 emissions shown in Figure 4-7 can only be used as a relative indicator of emissions during cyclic operation. NH_3 emission measurements made during cyclic operation indicated average emission rates were about one-third of the emission rates during NO_x-only operation. These results are discussed in detail in Section 4.3.

Because the NH_3/NO_x injection ratio can be used to vary the NO_x reduction efficiency without impacting SO_2 removal, it is possible to offset the effects of decreased acceptance times by increasing the quantity of NH_3 injected into the flue gas. However, the improvement in NO_x reduction efficiency which results is very limited. If the inlet SO_2 concentration increases above the design level, acceptance time would have to be reduced to maintain a constant SO_2 removal efficiency and NO_x reduction efficiency would decline. This could be offset by increased NH_3 injection for relatively small decreases in acceptance time but it would not be possible to offset significant decreases in acceptance time. The magnitude of the changes in acceptance which could be offset are relative and depend on the specific design of the SFGT process. However, it does appear that any design employed should be conservative and expect the maximum possible SO_2 concentration for the application.

4.1.5 Effects of NH_3 Injection Delay Time on Pilot Plant Performance

Prior to the start of the optimization tests, evidence indicated that delay of ammonia injection during the initial part of the acceptance period could improve NO_x reduction efficiency. Because the high temperatures which result from oxidation of the acceptor can promote oxidation of NH_3 to NO_x, delay of NH_3 injection during this period should reduce NH_3 oxidation and possibly improve the time averaged NO_x reduction efficiency.

The initial NH_3 injection delay tests were conducted while the plant processed air with injected pollutants and the results were favorable. The optimum NH_3 injection delay time was about 2 minutes and this resulted in about a 2 percent improvement in NO_x reduction efficiency. However, when tests were conducted while processing flue gas, the NH_3 injection delay time had little or no effect on NO_x reduction efficiency. As a result, the majority of tests conducted by UOP did not employ NH_3 injection delay.

4.1.6 The Effect of Partial Regeneration on Pilot Plant Performance

Partial regeneration of the acceptor is one technique of increasing NO_x reduction efficiency during the initial part of an acceptance period, thereby increasing the time averaged NO_x reduction efficiency. However, for a fixed reactor design, partial regeneration also results in a decrease in the time averaged SO_2 removal efficiency of the process. This is due to the decrease in the quantity of copper present as CuO during acceptance.

Partial regeneration was examined on a limited basis during optimization tests with the second acceptor. In these tests, approximately one seventh of acceptor was in the copper sulfate form following the regeneration step. With $CuSO_4$ present to catalyze the NO_x reduction reactions at the start of the acceptance period, a slight improvement in the time averaged NO_x reduction efficiency resulted. But, a significant decrease in SO_2 removal efficiency also occurred. These test results are shown in Table 4-3. Because the reduction in SO_2 removal was so great, partial regeneration was not examined further.

In a commercial application of an SFGT process, partial regeneration could be used to improve the time averaged NO_x reduction efficiency without impacting the SO_2 removal efficiency. This could be done by increasing the quantity of acceptor in the reactor to compensate for the unregenerated portion of the acceptor. However, this may not represent a cost effective approach to improving NO_x reduction efficiency. The costs for increased acceptor, larger reactors, etc., would have to be balanced against the costs of implementing other techniques for increasing the NO_x reduction efficiency of the process.

TABLE 4-3. IMPACT OF PARTIAL REGENERATION ON NO_x REDUCTION AND SO_2 REMOVAL.

Cycle	NO_x Reduction	SO_2 Removal	NH_3/NO_x Injection Ratio	Flowrate (Nm^3/hr)	Flue Gas Temperature (°C)
Complete Regeneration					
639	80.8	82.7	1.65	1330	404
643	82.2	81.4	1.53	1340	402
Partial Regeneration					
640	84.7	68.7	1.65	1340	407
644	84.9	70.7	1.57	1330	402

4.1.7 The Effects of Preoxidation on Pilot Plant Performance

The instantaneous NO_x reduction efficiency of the pilot plant at the start of an acceptance period was typically very poor. As a consequence, this reduced the time averaged NO_x reduction efficiency and made it difficult to obtain 90 percent NO_x reduction while maintaining SO_2 removal efficiency at 90 percent. The low NO_x reduction efficiencies at the start of acceptance were believed to be due, in part, to the lack of catalyst at the start of an acceptance period (elemental copper does not catalyze the NO_x reduction reactions). One technique for insuring catalyst is present at the start of acceptance is to leave a portion of the acceptor as $CuSO_4$. However, in the pilot plant, this resulted in a significant reduction in SO_2 removal efficiency and produced only a small increase NO_x reduction efficiency. Another technique for insuring catalyst is present at the start of acceptance is to insert a preoxidation step between acceptance and regeneration. Preoxidation converts the elemental copper to CuO (an active catalyst for NO_x reduction), prior to the start of an acceptance period.

A preoxidation step was included in the pilot plant operation during tests on the third acceptor. The results of these tests are summarized in Figure 4-8. As shown, the use of a preoxidation step had no significant effect on the NO_x reduction efficiency. These tests indicated that the initially poor NO_x removal was not due to a lack of catalyst but rather to some other factor.

Subsequent tests determined that the high temperature of the reactor internals caused the poor NO_x reduction efficiencies during the start of acceptance, apparently by promoting oxidation of NH_3. In these tests, the preoxidation step was followed by a cooling purge designed to return the reactor temperature to about 400°C following the highly exothermic oxidation reaction. The results of these tests are also summarized in Figure 4-8. As shown, the use of a cooling purge in combination with a preoxidation step improved NO_x reduction efficiency from 85 to 90 percent. It was during this series of tests that the pilot plant met the program objectives of 90 percent reduction in both NO_x and SO_2 emissions. It should be noted that the use of preoxidation and cooling did not significantly affect the SO_2 removal efficiency of the pilot plant.

Comparison of the preoxidation and cooling tests results with test results from typical operation reveal some interesting facts concerning the factors which limit NO_x reduction efficiencies at the start of an acceptance period. Figure 4-9 shows instantaneous reduction efficiency as a function of the $CuSO_4$ in the reactor for two tests: (1) typical operation in which regenerated acceptor containing elemental copper is exposed to flue gas, and (2) operation with a preoxidation and cooling step. If no temperature effects were present, the curves should be identical, assuming all other operating conditions are constant. However, as shown, there is a marked difference in the two curves. It appears that temperature impacts the NO_x reduction efficiency for up to 40 minutes of the acceptance period with the most significant effects occurring early in acceptance. This indicates that NO_x reduction efficiency during cyclic operation is largely a function of the rate at which the acceptor cools after oxidation.

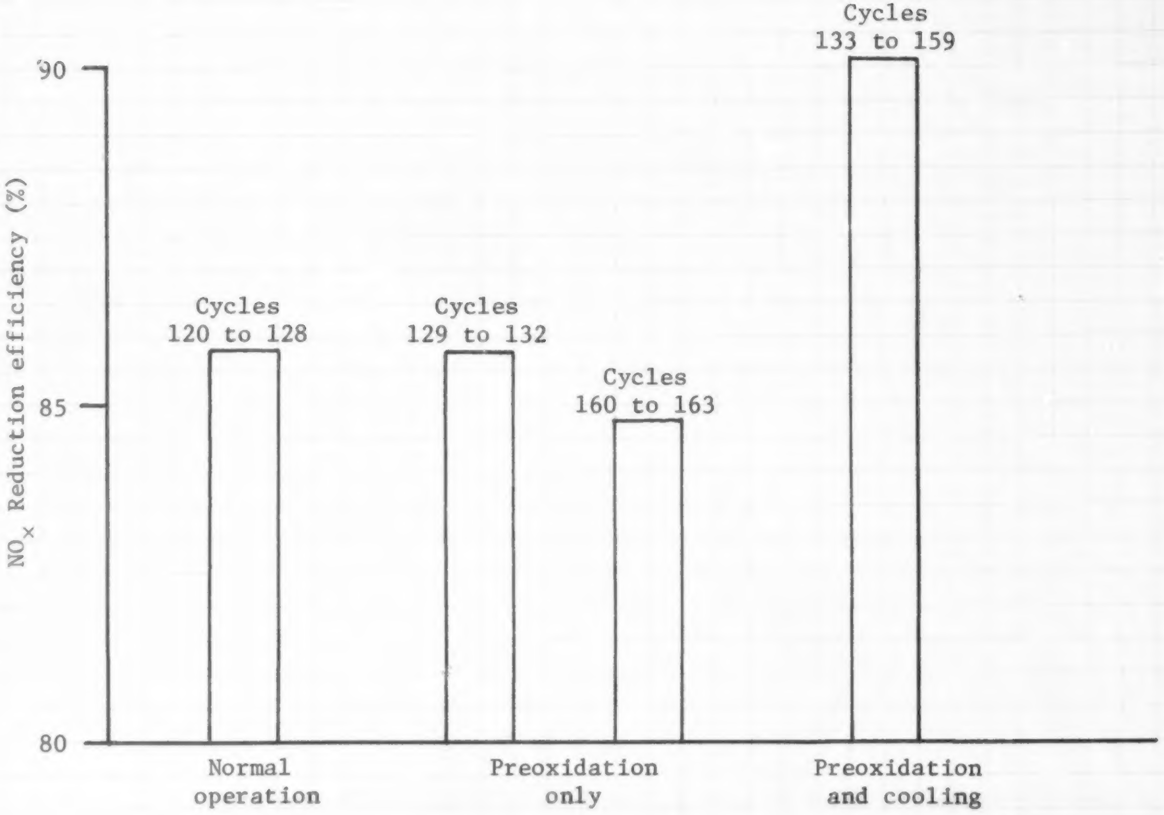

Figure 4-8. The effects of preoxidation and cooling on NO_x reduction efficiency

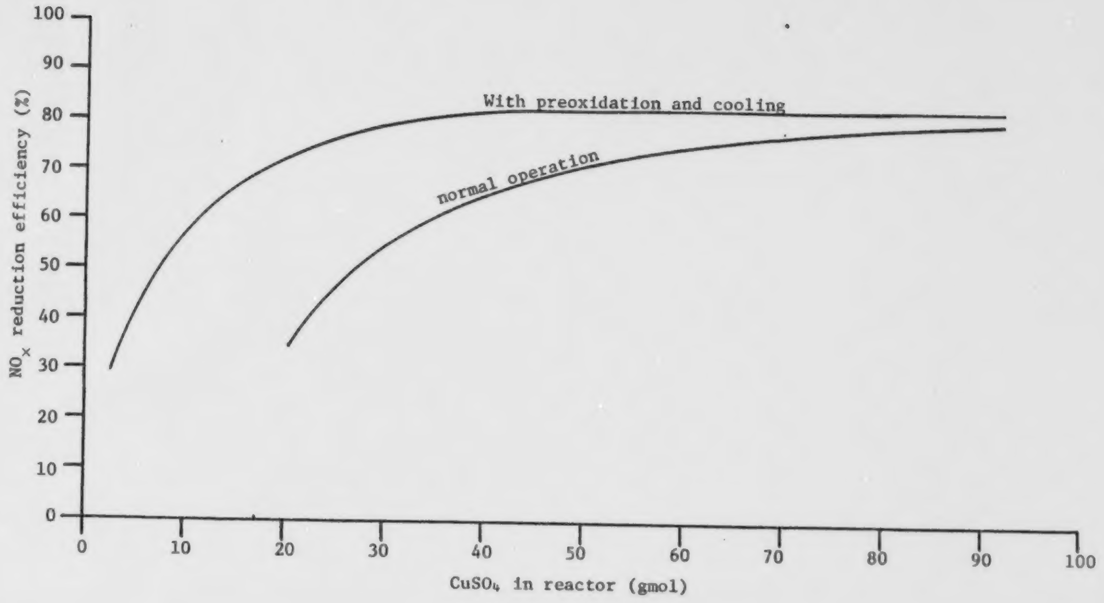

Figure 4-9. NO$_x$ reduction efficiency as a function of CuSO$_4$ in the reactor.

Although preoxidation and cooling significantly improved the performance of the SFGT pilot plant, it may not represent the optimum method of achieving high NO_x reduction efficiencies in a commercial application. In fact, UOP has indicated that they would not propose to use a preoxidation and cooling step in a commercial design. Problems with its use include added process complexity to permit passing oxidizing/cooling gas through a regenerated reactor and the requirements for heat recovery from the cooling gas. In addition, the use of an oxidation/cooling step effectively lengthens the regeneration period. If continuous processing of flue gas is required, as expected in a utility application, a longer regeneration period could require the reactor be designed for a longer acceptance period. This would require more acceptor overall.

The techniques used for preoxidation and cooling the acceptor in the pilot plant tests do not represent those which would be used if preoxidation/cooling were included in a commercial design. As a consequence it is very difficult to quantify the impact of preoxidation/cooling on a commercial design. It should be recognized that this represents one technique which may be considered for improving the NO_x reduction efficiencies measured in the pilot plant tests, but it may not represent the most cost effective one.

4.2 DEMONSTRATION TEST RESULTS

Originally, one demonstration test was scheduled as part of the SFGT pilot plant program. Its primary objective was to operate the pilot unit continuously for 90 days while reducing both NO_x and SO_2 emissions by 90 percent. However, because the pilot plant configuration of the SFGT process had difficulty meeting the performance levels of 90 percent NO_x reduction and 90 percent SO_2 removal, the demonstration test objectives were modified and two demonstration tests were conducted. In the first of these tests, the process was operated in a cyclic manner to reduce emissions of both NO_x and SO_2. The objective of this test was to operate continuously while reducing SO_2 emissions by 90 percent. The NO_x reduction efficiency during these tests was a dependent variable constrained by a maximum NH_3/NO_x ratio of 1.25. In the second demonstration test, the reactor was not regenerated. Instead, it was operated as a typical SCR process with no SO_2 removal. The objective of this test was to reduce NO_x emissions by 90 percent.

The following discussion summarizes the results of the two demonstration tests conducted by UOP. This includes quantification of typical operating conditions during the demonstration tests and a discussion of the quality of the data. The discussion also examines the implications of these results on a potential commercial application of the SFGT process to a coal-fired utility boiler.

4.2.1 NO_x/SO_2 Demonstration Test

The first demonstration test was conducted during June, 1980. The primary objective of this test was to operate the pilot unit under conditions which resulted in 90 percent SO_2 removal without regard for the NO_x reduction efficiency achieved. Some secondary objectives of the test were to characterize key process operating parameters under conditions in which the independent operating variables were maintained constant. For the most part, the objectives of this demonstration test were met. For 17 of 22 days in which 75 percent of the operating data were collected, the SO_2 removal averaged 90.4 percent. The operating parameter which was varied to achieve this objective was the length of the acceptance period. This caused some variation in other operating parameters. However, on the average, the operating parameters remained relatively constant throughout the demonstration test. The demonstration test results, coupled with the results of selected optimization tests, also indicated that the acceptor activity remained relatively constant after an initial decline upon exposure to flue gas.

The following discussion examines the results of the NO_x/SO_2 demonstration test including a discussion of how the test results influence a commercial application of the SFGT process.

Operating Parameter Levels

Figure 4-10 presents the 24-hour averages of NO_x and SO_2 reduction efficiencies and acceptance time during the demonstration test. As shown, the average SO_2 removal remained relatively constant at 90 percent, but the NO_x reduction efficiency declines over the duration test. This decline was due to a decrease in the acceptance time which was required to maintain SO_2 removal efficiency at 90 percent. Initially this decline appeared to be due to loss of acceptor activity, but it was also accompanied by a gradual increase in pressure drop across the reactor.

Assuming the pressure drop is less than 10 percent of the total pressure of the gas, the relationship between reactor pressure drop and reactor flowrate is given by Equation 4-1.

$$\text{Flow} \propto (\Delta P)^{\frac{1}{2}} \qquad (4\text{-}1)$$

The measured reactor flowrate did not change during this period but quality assurance audits indicated an increased error between UOP's and Radian's measured flowrates. Subsequent investigation revealed that fly ash had interfered with the measurement of the pressure drop across the venturi inaccurate flowrate measurements during a portion of the demonstration test. Apparently a greater than measured amount of flue gas was entering the reactor requiring shorter acceptance times to maintain 90 percent SO_2 removal. After the fly ash interference was eliminated, reactor performance was similar to that at the start of the demonstration test.

The fact that the flue gas flowrate measurements were inaccurate during part of the NO_x/SO_2 demonstration test makes some of the calculated process parameters inaccurate since they were based on an incorrect flowrate. However, on the average, the key process parameters remained relatively constant and they appear representative of typical levels for the SFGT process. Table 4-4 presents the mean value and standard deviations for key process operating parameters during the NO_x/SO_2 demonstration test. As shown, the standard

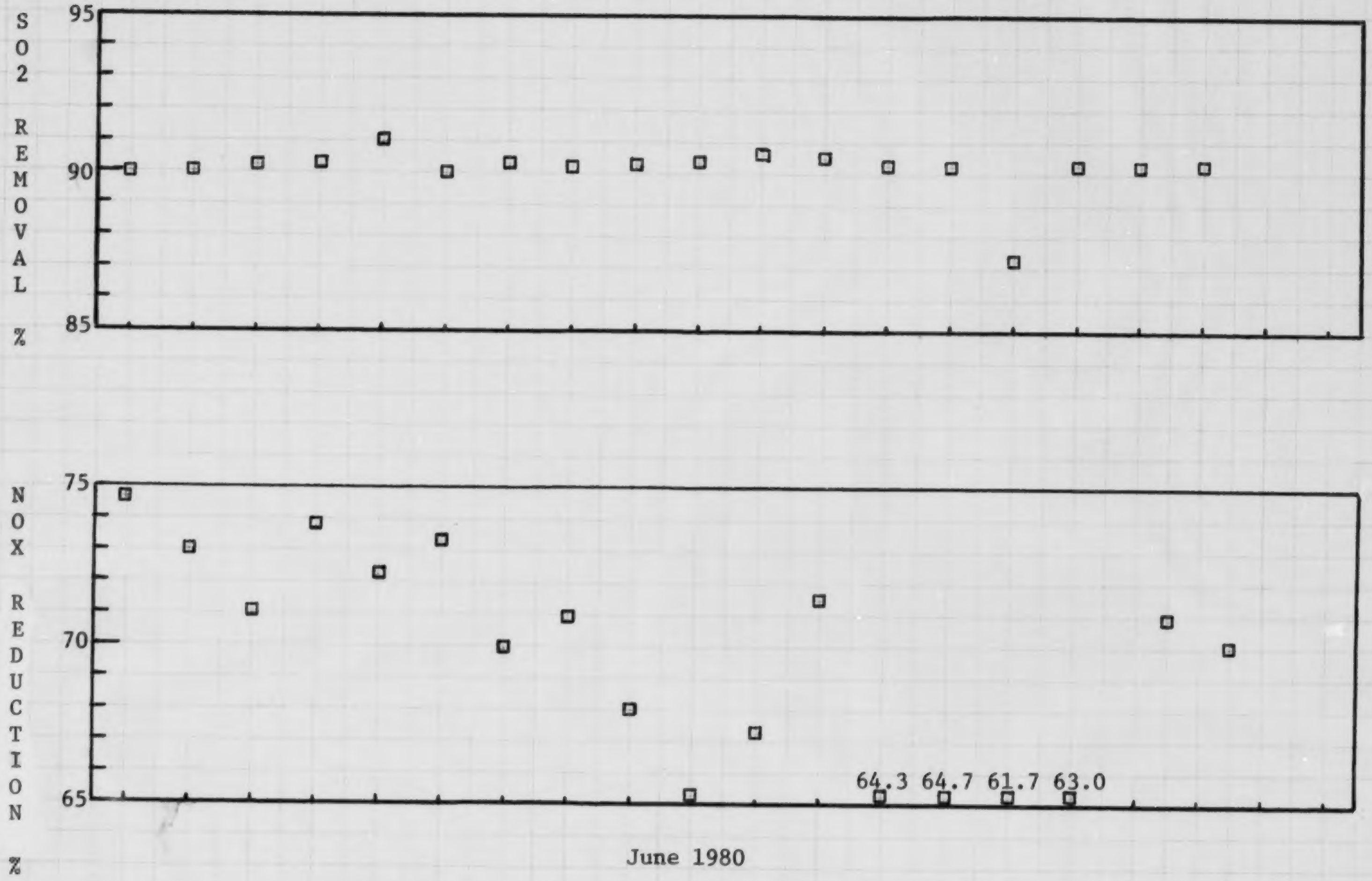

Figure 4-10. Demonstration test results from the Shell Flue Gas Treatment pilot plant.

deviations are relatively low, indicating that the key operating parameters did not vary significantly during the demonstration test. The principal exceptions are NO_x removal and acceptance time which of course are related. Other variables with relatively large standard deviations are the NO_x and SO_2 inlet concentrations which could not be controlled. Because most of the operating parameters were constant, they were used as the basis for material balance calculations presented in Section 5 of this report.

TABLE 4-4 KEY OPERATING PARAMETER LEVELS DURING THE NO_x/SO_2 DEMONSTRATION TEST

Operating Parameter	Mean Value	Standard Deviation
Reactor feed rate (Nm^3/hr)	1592	18.1
Acceptance time (min)	62.3	5.76
Regeneration time (min)	27.9	1.16
Inlet SO_2 concentration (ppm)	2413	99.5
SO_2 removal (%)	90.2	1.0
Sulfur weight recovery (%)	101.4	7.45
Inlet NO_x concentration (ppm)	368	45.9
NO_x removal (%)	69.1	5.2
NH_3/NO_x injection ratio	1.24	0.08
Flue gas/reactor inlet temp. (°C)	411	3.9
Reactor pressure drop (kPa)	2.24	0.25
H_2/SO_2 feed ratio	4.15	0.42
Steam rate for regeneration (Nm^3/hr)	129.6	1.7
Regeneration out flow (Nm^3/hr)	165.4	1.7

As evident from the preceding discussion, the SFGT pilot plant successfully met the modified objectives of the NO_x/SO_2 demonstration test. The ability of the process to achieve an SO_2 removal efficiency of 90 percent was demonstrated. However, NO_x reduction efficiency was below the original target performance level of 90 percent. This indicates that, under the operating conditions during the demonstration test, the design of the pilot unit was not suitable for achieving simultaneous reduction of NO_x and SO_2 emissions by 90 percent. Modification of the process design and/or operation will be required to meet this performance level on a commercial system.

Acceptor Activity

Much of the data gathered during the demonstration test are characteristic of a commercial application of the SFGT process. However, there is one significant aspect of process performance which was not resolved by the demonstration test. Due to its short duration, the demonstration test did not establish the ability of the acceptor to maintain constant activity with respect to both NO_x reduction and SO_2 removal for a period equivalent to 1 year's operation. The total operating time on the second acceptor did, however, indicate that acceptor activity was relatively stable after an initial decline upon exposure to flue gas.

Figure 4-11 shows the relative activity of the second acceptor as a function of time flue gas was processed. Relative activity was determined by the ratio of SO_2 removals at different times under identical operating conditions. The figure is divided into two parts which represent the addition of a seventh cell of acceptor to the reactor. Upon addition of this seventh cell, the relative activity was set at 1.0 again, although a large percentage of the acceptor had processed flue gas for over 200 hours.

As shown by Figure 4-11, after an initial drop, the acceptor activity remained constant for 240 hours of flue gas operation. The addition of the seventh cell also resulted in an initial drop in activity (although not as great as was observed with completely fresh acceptor) then constant performance was recorded for 460 hours of flue gas operation. This indicates that some of the

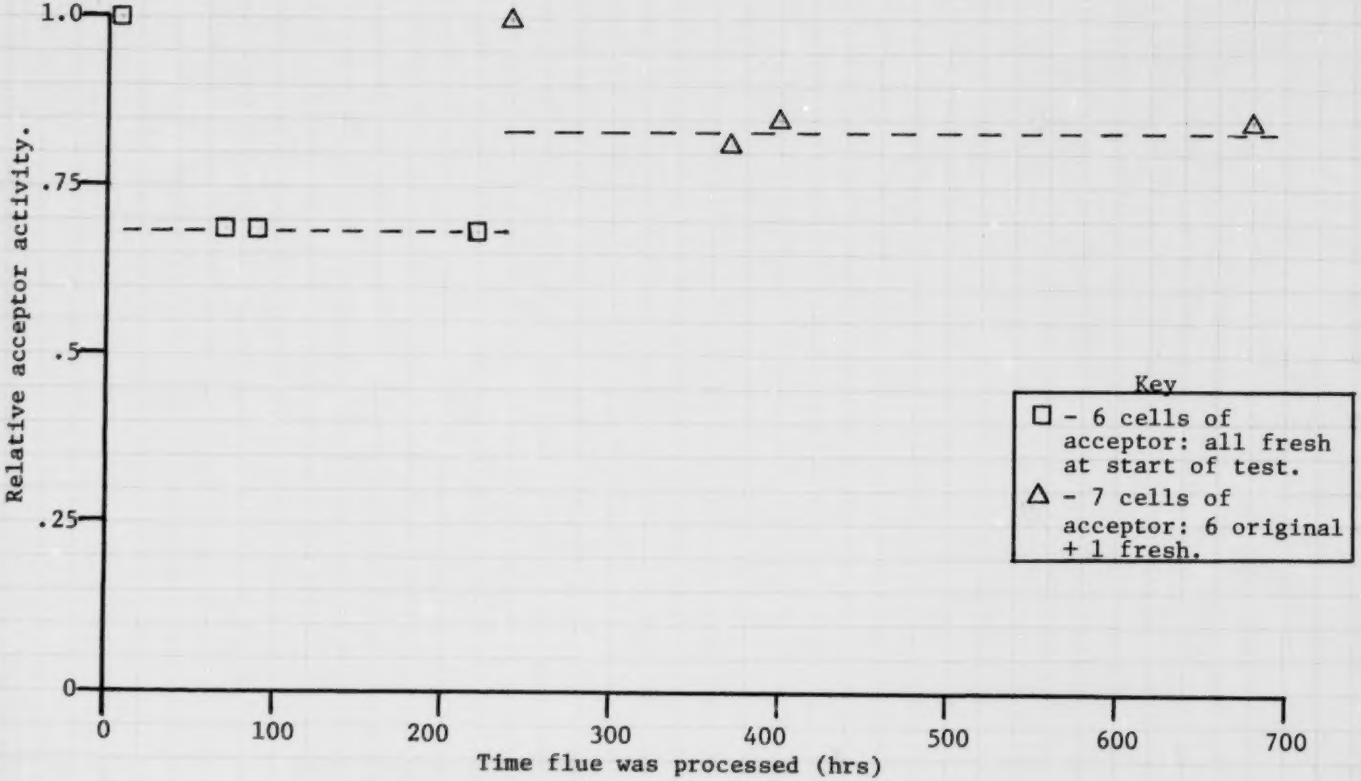

Figure 4-11. Relative activity of second acceptor tested.

acceptor (~80 percent) exhibited stable operation for approximately 700 hours of flue gas operation.

Although the data in Figure 4-11 indicate that acceptor appears stable when processing particulate laden flue gas from a coal fired boiler, these data only cover a period of 700 hours which is about one-eighth of one year's operating time. Without further tests, it is uncertain whether the acceptor would perform satisfactorily for a one year period.

Representative Slip Curves

In order to determine the quantity of acceptor required to achieve a specified reduction in NO_x and SO_2 emissions, it is necessary to quantify the instantaneous removal rates of these pollutants as a function of time. These rates are represented by "slip" curves which show NO_x and SO_2 concentrations at the reactor outlet throughout an acceptance period. Because most process operating parameters remained relatively constant during the NO_x/SO_2 demonstration test, the slip curves obtained during this test can be used to generate representative slip curves. These can, in turn, be used to complete a conceptual design of an SFGT process based on the results of the NO_x/SO_2 demonstration test.

Figures 4-12 and 4-13 present "representative" slip curves for NO_x and SO_2 which were developed from selected cycles during the demonstration tests. As shown, both SO_2 and NO_x concentrations in the reactor outlet follow the typical pattern discussed previously. The cycles used to develop these representative slip curves were selected such that test conditions were close to the mean value for all the cycles in the demonstration test. Table 4-5 compares the average values for all the cycles with those used to develop the "representative" slip curves. As shown, these averages are quite close for each operating parameter.

The slip curves presented in Figure 4-12 are those used to develop a conceptual design of the SFGT process in Section 5 of this report. As shown,

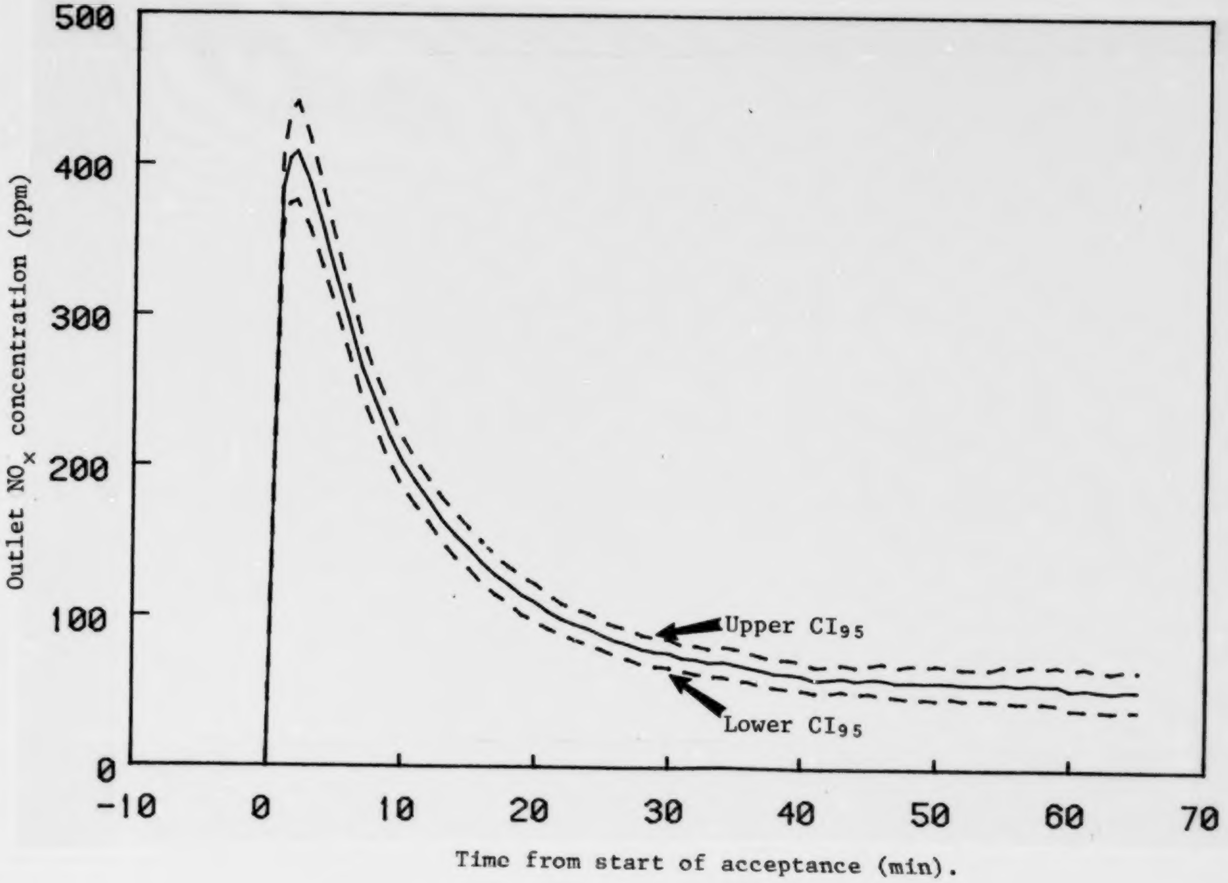

Figure 4-12. Representative NO_x slip curve from NO_x/SO_2 demonstration test.

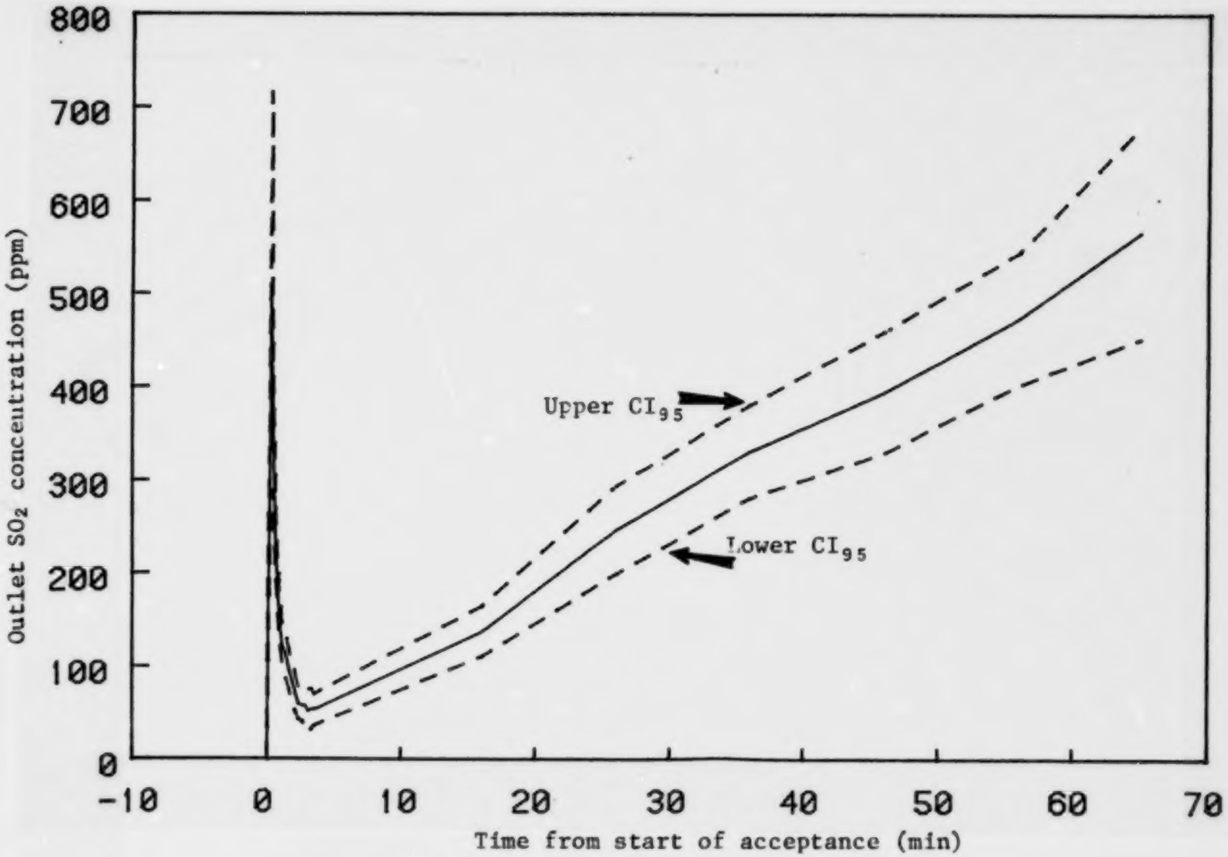

Figure 4-13. Representative SO_2 slip curve from NO_x/SO_2 demonstration test.

the NO_x emissions were very high at the start of the acceptance period, especially when compared to those observed during the preoxidation and cooling tests with the third acceptor. This results in the requirement for an extended acceptance period in the conceptual design which significantly increases the required acceptor inventory. This is discussed in more detail in Section 5.

TAPLE 4-5. A COMPARISON OF THE MEAN VALUES OF KEY OPERATING PARAMETERS FROM THE NO_x/SO_2 DEMONSTRATION TEST WITH THOSE FROM TESTS USED TO DEVELOP REPRESENTATIVE SLIP CURVES.

	Mean Value	
Parameter	Demonstration Test	Representative Slip Curved
Reactor feed rate (Nm^3/hr)	1592	1587
Acceptance time (min)	62.3	63.3
Regeneration time (min)	27.9	28.4
Inlet SO_2 concentration (ppm)	2413	2418
SO_2 removal (%)	90.2	90.1
Sulfur weight recovery	101.4	104.5
Inlet NO_x concentration	368.4	374.4
NO_x removal (%)	69.1	70.1
NH_3/NO_x injection ratio	1.24	1.25
Flue gas/reactor inlet temp (°C)	411.4	409.3
Reactor pressure drop (kPa)	2.24	2.05
H_2/SO_2 feed ratio	4.15	3.83
Steam for regeneration (Nm^3/hr)	129.5	129.4
Regeneration out flow (Nm^3/hr)	165.6	165.5

4.2.2 NO_x-Only Demonstration Test

The NO_x-only demonstration test was conducted during July and August 1980. The objective of this test was to operate the pilot unit continuously for 30 days while reducing NO_x emissions by 90 percent at a minimum NH_3/NO_x ratio. A secondary objective was to characterize the NH_3 emissions from the process.

During the NO_x-only demonstration test the pilot plant was operated for 35 days with a minimum of 75 percent of the data collected for 31 of the 35 days. For the 31 "compliance days" NO_x removal averaged 89.5 percent at an NH_3/NO_x injection ratio of 1.26. Throughout this period, all process operating parameters remained relatively constant. This can be seen by examining the mean values and standard deviation of key process operating parameters for the NO_x-only demonstration tests which are presented in Table 4-6.

TABLE 4-6. KEY OPERATING PARAMETER LEVELS DURING THE NO_x-ONLY DEMONSTRATION TEST

Operating Parameter	Mean Value	Standard Deviation
NO_x Removal (%)	89.13	4.15
Reactor Pressure Drop (kPa)	2.08	0.56
Flue Gas/Reactor Inlet Temperature (°C)	413.7	[illegible]
NH_3/NO_x Injection Ratio	1.26	0.12
Inlet NO_x Concentration (ppm)	366.7	82.19
Inlet SO_2 Concentration (ppm)	39.5	17.29
SO_2 Concentration (ppm)	2.549	16.27

Figure 4-14 shows the 24-hour averages of NO_x removal efficiency and the NH_3/NO_x injection ratio during the demonstration test. Although these data indicate that the objectives of the demonstration test were not met, they do show that 90 percent or greater NO_x reduction was achieved for the

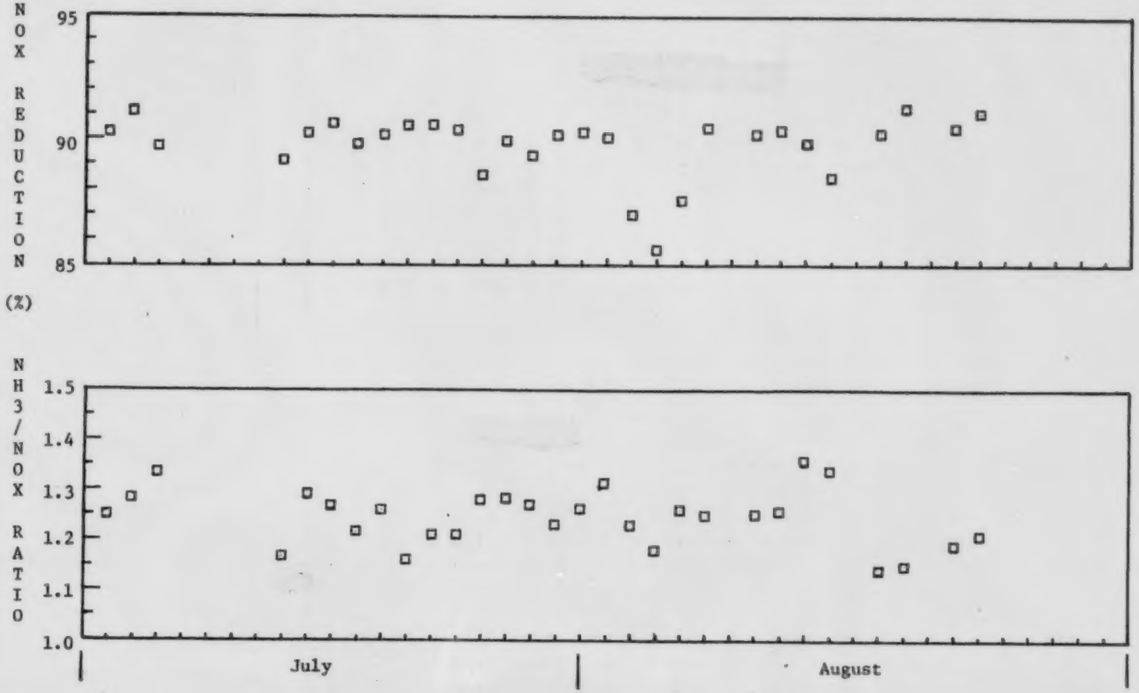

Figure 4-14. Results of the NO_x-only demonstration test at the Shell Flue Gas Treatment pilot plant.

majority of the time. The principal reason overall NO_x reduction was less than 90 percent was due to the NH_3/NO_x injection ratio being too low. UOP attempted to maintain the NO_x reduction efficiency just at the 90 percent level, thus minimizing NH_3 consumption. However, the average NH_3/NO_x injection ratio was not quite high enough to result in 90 percent average NO_x reduction.

The secondary objective of measuring NH_3 emissions during the NO_x-only demonstration test was not met either. UOP attempted to use a TECO chemiluminescent analyzer to measure total nitrogen (i.e., NH_3 and NO_x) in the reactor outlet and thus determine the NH_3 concentration by difference between total nitrogen and the outlet NO_x monitor. However, the total nitrogen analyzer's performance was erratic and was never in agreement with batch sampling and analysis for NH_3 emissions. In fact, the total nitrogen analyzer often gave readings below those of the NO_x monitor. Although continuous NH_3 analysis was not possible, both UOP and Radian completed batch sampling and analysis for NH_3 emissions from the reactor. The results of this work are discussed in Section 4.1 and 4.3.

The results of the NO_x-only tests with the SFGT pilot unit indicated that the process is capable of achieving 90 percent NO_x reduction. However, these test results do not have much significance in terms of commercial application of the SFGT process for simultaneous reduction of NO_x and SO_x.

4.3 QUALITY ASSURANCE AUDIT RESULTS

The QA audits conducted by Radian were designed to insure that the process data required to characterize the operation of the SFGT pilot plant were accurate. Radian employed reference methods for auditing process operating parameters which were measured on a continuous or routine basis by UOP. One exception to this was the measurement of NH_3 emissions which were not routinely monitored by UOP, although the original design of the pilot unit included an analyzer intended to determine NH_3 emission rates.

The results of the NH_3 emissions sampling are presented in Table 4-7. Samples were collected during both NO_x/SO_2 tests and NO_x-only tests. As shown, the samples taken during the NO_x-only tests indicate relatively high NH_3 emissions which averaged 49 ppm, but the samples collected during NO_x/SO_2 tests resulted in significantly different NH_3 emissions. NH_3 emission samples were collected over the entire acceptance period during cyclic operation indicating an average NH_3 concentration at the reactor outlet of 15 ppm, which is less than one-third the emissions during NO_x-only operation

There are several possible explanations for the difference between the NH_3 emissions during NO_x/SO_2 and NO_x-only operation. The most consistent explanation is that oxidation of NH_3 during the initial part of the acceptance period reduced time averaged emissions. The initially high temperatures in the reactor have been shown to lower NO_x removal efficiencies for up to 40 minutes in the acceptance cycle (Section 4.1.7). It is likely that this is due to the NH_3 oxidation and it would be anticipated that NH_3 emissions would be lower due to oxidation. It should be noted that the NH_3 emissions measured during cyclic operation represent an integrated average over an entire acceptance period and, thus, do not provide information concerning the instantaneous NH_3 emissions over an acceptance period. It is possible that the NH_3 emission rate changes as a function of acceptance time, especially if NH_3 oxidation is the cause of the relatively low NH_3 emission rates during cyclic operation.

TABLE 4-7. SFGT PILOT PLANT NH_3 EMISSIONS

Date	Time	UOP Cycle #	NO_x In (ppm dry)	NH_3:NO_x	NH_3 Emissions (ppm dry)
6-21	16:12 - 17:12	875	380	1.17	15
6-23	12:49 - 13:52	903	420	1.21	16
6-24	13:26 - 14:36	918	390	1.31	22
6-26	13:23 - 14:20	948	375	1.25	17
6-26	17:52 - 18:48	951	–	–	16
6-27	15:06 - 16:02	965	–	–	11
6-28	15:49 - 16:52	982	392	1.17	12
6-28	17:27 - 18:32	983	402	1.19	13
6-30	15:27 - 17:06	1004	–	–	16
7-11	14:01 - 14:23	NO_xOnly	420	1.18	47
7-15	14:50 - 15:15	NO_xOnly	327	1.21	52
7-15	18:28 - 18:53	NO_xOnly	224	1.38	48

The results of the other QA audits conducted by Radian are summarized in Table 4-8. Table 4-8 also identifies the technique used to conduct the audits. (For additional details, including the results of individual audits, see Appendix A). As shown, all but the flue gas flowrate measurements were within 10 percent of the values recorded by UOP. As discussed earlier, it was not possible to conduct an independent audit of steam flow or H_2 flow during the QA program since this would have necessitated shutting down operation of the pilot unit during the demonstration test.

TABLE 4-8. QA AUDIT RESULTS

Measurement Audited	Audit Procedure	Relative[1] Error (%)
Flue gas flowrate	EPA Reference Method 2	-14.4
NH_3 injection rate	Absorption followed by weight gain measurement - (analogous to EPA method 4)	7.6
Reactor pressure drop	Magnehelic differential pressure gauge	-1.4
Reactor inlet temp.	Thermocouple with traverse of reactor inlet	-1.3
H_2 flowrate	NA[2]	-
Steam flowrate	NA[2]	-

[1] Relative error = $\frac{\text{(Process measurement - Audit result)}}{\text{(Audit result)}} \times 100\%$

[2] These measurements were not audited due to difficulty in accessing process streams.

In general, the QA audit results indicate that the process data collected by UOP accurately characterize the operation of the SFGT pilot plant. However, the discrepancy in the flowrate measurements indicated there could be a problem with this measurement technique and the reactor may have been processing flue gas at greater than design flowrates. For the most part, the difference between the flowrate audit results and the flowrate measurement was constant indicating a constant error was being made, either by the venturi flow meter or in the reference analysis. In subsequent tests, UOP confirmed the accuracy of the venturi meter by an independent test in which a known quantity of SO_2 was injected into air and the resultant concentration at the reactor inlet measured. This technique gave flowrates which were within 5 percent of the venturi. Apparently there was a consistent error in the reference method used by Radian to conduct the QA audit. The most likely explanation of this error was an inaccurate measurement of the duct diameter where the pitot tube was used to measure flue gas velocity. Since velocity is measured directly by the reference method and the flowrate is calculated, an inaccurate value for the duct diameter would cause a constant error in the results of the flowrate audit.

Based on the results of the QA audits and subsequent tests by UOP, the major process measurements made by UOP were accurate within the limits of the techniques employed to make the measurements. Consequently, UOP's process data can be used to characterize operation of the process without the use of a correction factor. However, because of the relatively small size of the process streams in the pilot unit, good design practice would dictate that the most conservative of the 95 percent confidence interval be used in developing a conceptual design for a commercial application of the SFGT process. The 95 percent confidence intervals were calculated for each of the key process operating parameters discussed in Section 4.2.1 and are presented in Table 4-9. These values were used in completing the heat and material balances presented in Section 5 of this report.

TABLE 4-9. 95 PERCENT CONFIDENCE INTERVAL FOR KEY OPERATING PARAMETERS

Operating Parameter	95 Percent Confidence Interval
Reactor feed rate (Nm^3/hr)	$1589 \leq x \leq 1595$
Acceptance time (min)	$61.5 \leq x \leq 63.1$
Regeneration time (min)	$27.7 \leq x \leq 28.1$
Inlet SO_2 concentration (ppm)	$2398 \leq x \leq 2428$
SO_2 removal (%)	$90.1 \leq x \leq 90.3$
Sulfur weight recovery (%)	$100.3 \leq x \leq 102.5$
Inlet NO_x concentration (ppm)	$361 \leq x \leq 375$
NO_x removal (%)	$58.3 \leq x \leq 69.9$
NH_3/NO_x injection ratio	$1.23 \leq x \leq 1.25$
Flue gas/reactor inlet temperature (°C)	$411 \leq x \leq 412$
Reactor pressure drop (KPa)	$2.20 \leq x \leq 2.28$
H_2/SO_2 feed ratio	$4.09 \leq x \leq 4.21$
Steam rate for regeneration (Nm^3/hr)	$129.3 \leq x \leq 129.9$
Regeneration out flowrate (Nm^3/hr)	$165.1 \leq x \leq 165.7$

4.4 SECONDARY EMISSIONS SAMPLING RESULTS

The secondary emissions sampling program was conducted by Radian during June and July 1980, concurrent with the demonstration tests conducted by UOP. The objective of this part of Radian's test program was to quantify changes in the emission rates of pollutants other than NO_x or SO_2 across the SFGT reactor. For the most part, these tests were conducted during tests in which both NO_x and SO_2 were being removed from the flue gas (cyclic operation), and the data collected were used in completing a material balance for a conceptual design of the SFGT process.

Table 4-10 summarizes the results of the secondary emissions sampling program at the SFGT pilot plant. As shown, concentrations of both hydrogen cyanide (HCN) and nitrosoamines were below the detection limits of the analytical technique used in the test program. For HCN, this detection limit is equivalent to less than 10 ppbv and for N-Nitrosodimethylamine, less than 2 ppbv.

Decreases in both the HC and CO concentrations were measured across the reactor. This change was probably due to oxidation of these pollutants in the reactor. It is believed that the relatively high levels of CO and HC's measured at the inlet were due to emissions from the in-line propane burners located upstream of the reactor. Table 4-10 also shows that a decrease in SO_3 concentration was also measured across the reactor. This decrease is due to removal of SO_3 from the flue gas via reaction with the acceptor. The apparent change in particulate concentration shown in the table is believed to be due to unaccounted for stratification in the ducts. It should be noted that no results for N_2O are presented. This is due to the fact that the analytical technique used to measure N_2O proved unsatisfactory for use in a flue gas stream.

The following discussion presents the stack sampling results in more detail. This includes an examination of the impact of the stack sampling results on a commercial application of the SFGT process.

TABLE 4-10. STACK SAMPLING RESULTS AT THE SFGT PILOT PLANT

Flue Gas Component	Reactor Inlet Concentration[1]	Reactor Outlet Concentration[1]	Measurement Technique
Nitrosoamines[2]	<5 μg/dscm[3]	<5 μg/dscm	Absorption, extraction, gas chromatograph w/nitrogen specific detector
Cyanides[2]	<.01 mg/dscm	<.01 mg/dscm	Absorption, distillation, titration
Sulfur trioxide	11.4 ppmv (dry basis)	0.1 ppmv (dry basis)	Controlled condensation, ion chromatograph
Hydrocarbons (C_1-C_6)	28.5 ppmv	21.0 ppmv	Gas chromatograph flame ionization detector
Carbon monoxide	0.13%	<0.017%[2]	Fischer gas partitioner
Particulates	8.9 gm/dscm	6.3 gm/dscm	In stack filter

[1] Average of 2 or more tests
[2] Below the detection limit
[3] dscm = dry standard cubic meters

Sulfur Trioxide

Samples were collected at the reactor inlet and outlet to determine if the SFGT process removed SO_3 in addition to SO_2. Originally, six sets of SO_3 analyses were scheduled. However, as a result of several boiler outages, only 2 sets of samples were obtained before the test program was concluded. The results of each SO_3 analysis are presented in Table 4-11. As shown, the analyses were consistent, indicating almost complete removal of SO_3 from the flue gas. The results should be used with caution, however, because of the small number of tests.

TABLE 4-11. CHANGE IN SO_3 CONCENTRATION ACROSS THE REACTOR AT THE SFGT PILOT PLANT

Date	Time	SO_3 Inlet (ppm dry)	SO_3 Outlet (ppm dry)	Removal %
10-8	14:40 - 15:40	10.4	0.095	99.1
10-8	17:15 - 18:45	12.4	0.108	99.1

The fact that the SFGT process removes most of the SO_3 from flue gas has a significant impact on a commercial application of the SFGT process. This results in lowering the H_2SO_4 dewpoint of the flue gas which increases the potential for heat recovery in an air preheater without the adverse effects of downstream corrosion. For the flue gas at the SFGT pilot unit, the acid dewpoint was lowered from 145 to about 110°C which represents an additional 9 kcal per kilogram of flue gas which could potentially be recovered in the air preheater. However, other constraints may limit the fraction of this heat which can be recovered.

Another benefit which results from reduced SO_3 emissions is a reduction in the potential for formation of ammonium sulfates in the air preheater. Experience in Japan has shown that NH_3 emitted from an SCR system can react with SO_3 present in the flue gas and cause plugging and corrosion of the preheater. Removal of SO_3 from the gas stream will minimize this problem.[4] The The NH_3 may also react with any HCl present, but since this compound exists only as a solid, it should not present a problem in the air preheater.[4,5]

Particulates

Particulate samples were collected at the inlet and outlet of the reactor for two reasons. First, particulate concentrations were measured to document the particulate levels the reactor was exposed to. Second, elemental analysis of the reactor inlet and outlet samples was completed to determine if a change occurred in the particulate composition across the reactor due to acceptor attrition.

The results of the particulate concentration measurements made at the SFGT plant are presented in Table 4-12. As shown, particulate concentrations averaged 8.9 gm/dscm at the inlet and 6.3 gm/dscm at the outlet. The reactor operated under positive pressure so no leaks were present in the system to dilute the flue gas. Therefore, it appears that the 29 percent difference in particulate concentrations is due to an error in sampling. The fact that the difference is relatively constant in each test suggests a systematic error in the sampling procedure. Because of the location of sample ports on the SFGT pilot unit, it was only possible to traverse the duct in a single plane. Since the sample ports were also located close to disturbances at the SFGT plant, it is conceivable that representative sampling of the duct was not possible using this single plane.

TABLE 4-12. PARTICULATE CONCENTRATIONS MEASURED AT SFGT PILOT PLANT

Date	Time	Inlet (gm/dscm)	Outlet (gm/dscm)
6-19	10:47 - 11:27	8.3	6.7
6-19	13:55 - 14:35	11.2	6.8
6-19	17:05 - 17:45	7.4	5.5

Table 4-13 presents the results of the elemental analysis of the particulates collected at the SFGT pilot plant. This analysis was conducted to determine if acceptor erosion was causing an increase in the concentration of Alumina (Al) or Copper (Cu) in the particulates leaving the reactor. As shown, no significant change in the composition of the particulates was measured with respect to these elements. The changes which are shown in Table 4-13 are probably due to random errors in the sampling or analysis technique and are not representative of real changes in particulate composition. Therefore, it can be concluded that no significant increase in the concentrations of Al or Cu in the particulates occurred due to catalyst erosion. This does not indicate that erosion is not occurring, only that the rate of erosion does not produce a significant change (greater than 10 percent) in the particulate composition.

The particulate sampling results indicate that a commercial application of the SFGT process can operate under high particulate concentrations without plugging the reactor bed or causing measurable changes in the particulate composition. However, due to the limited time flue gas was processed in the SFGT pilot plant, no conclusions can be drawn concerning the long-term stability of the acceptor when exposed to high particulate concentrations.

TABLE 4-13. RESULTS OF PARTICULATE ANALYSIS AT THE SFGT PILOT PLANT[1]

Component	In	Out	Out/In
Al	8.6%	8.0%	.93
Ca	1.8%	1.8%	1.00
Fe	12%	11.1%	0.93
K	1.5%	1.4%	0.93
Mg	5100 ppm	5000 ppm	0.98
Mn	300 ppm	320 ppm	1.07
Sn	270 ppm	270 ppm	1.00
Na	4300 ppm	5100 ppm	1.19
Si	20%	16%	0.80
Zn	410 ppm	720 ppm	1.76
Cu	96 ppm	100 ppm	1.04
Ti	5400 ppm	5100 ppm	0.94
V	255 ppm	340 ppm	1.33

[1] Concentrations are on a mass fraction basis

Carbon Monoxide and Hydrocarbons

Samples were collected and analyzed for carbon monoxide and hydrocarbons at the inlet and outlet of the reactor. The results of these analyses show a decrease in the concentrations of both CO and HC's across the reactor. This decrease is attributed to catalytic oxidation of the CO and HC's to form CO_2 and H_2O. The oxidation of these compounds was not unexpected since the NO_x reduction reaction is actually an oxidation of NH_3 by NO_x and the catalyst is basically an oxidation catalyst. It should be noted that the high levels of CO and HC's at the SFGT pilot plant were probably a result of incomplete combustion in the propane burners used for flue gas temperature control upstream of the reactor.

Because the SFGT process reduces emission rates of CO and HC's, an additional environmental benefit results from application of the process. However, this does not have a significant effect on the economics or applicability of the process since CO and HC emissions are not typically a problem in utility boilers.

Hydrogen Cyanide

Samples were collected and analyzed to determine if NH_3 was reacting with hydrocarbons in the reactor forming HCN. Samples collected at both the reactor inlet and outlet were below the detection of the analytical technique employed. While this does not indicate whether or not HCN was being produced in the reactor, the maximum possible HCN concentration in the flue gas exiting the reactor was 10 ppb. This is far below the threshold limit value (TLV) of 10 ppm, a concentration considered safe for worker exposure.[6] Therefore, the secondary emissions sampling results indicate that HCN production is not a problem with the SFGT process.

Nitrosoamines

Samples were collected and analyzed for nitrosoamines at the inlet and outlet of the SFGT reactor to determine if NH_3 was reacting with other flue gas components forming nitrosoamine compounds. As with HCN, samples collected at both the reactor inlet and outlet were below the detection limit of the analytical technique employed. While these results do not conclusively show that nitrosoamines are not produced in the reactor, the maximum possible concentration in the flue gas leaving the reactor was 5 $\mu g/m^3$. This is well below the 65 $\mu g/m^3$* source concentration considered safe by EPA's multimedia environmental goals (MEG's) although considerably greater than the safe ambient level (.155 $\mu g/m^3$).[6] With dispersion, the maximum of 5 $\mu g/m^3$ in the stack gas exiting the reactor should result in ambient concentrations well below the safe ambient level. These results indicate that nitrosoamine production (if any) in the SFGT reactor should not present an environmental problem.

Nitrous Oxide

Nitrous oxide is one possible product of the reactions between NO_x and NH_3 as shown in Equation 4-2.

$$6NO + 2NH_3 \rightarrow 3N_2O + 3H_2O + N_2 \qquad (4-2)$$

Samples were collected at the inlet and outlet of the SFGT reactor to determine if significant quantities of N_2O were being produced. Unfortunately, the method used in the sampling program was not sensitive enough to detect the presence of N_2O (if any) in the reactor effluent. Several interfering peaks combined with the low level of any N_2O present made determination of the N_2O concentration impossible.

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*The values given are for N-Nitrosodimethylamine which has the lowest safe levels of all the aliphatic nitrosoamines.

Although N_2O is not currently considered an environmental hazard, it is possible that future regulatory action may limit emission rates of this compound. Therefore, any further development work on the SFGT process should include sampling designed to characterize N_2O emissions from the reactor. A technique which appears suitable for measuring N_2O emissions is described in Appendix B of this report along with a description of the technique which proved unsuccessful during the secondary emissions sampling program.

Summary

The stack sampling program conducted by Radian was designed to quantify changes in the emission rate of secondary pollutants from the SFGT process. The results of this program showed that:

- The SFGT process removes nearly all the SO_3 in the flue gas entering the reactor. This could have a beneficial impact on downstream equipment which may be subject to acid corrosion.
- The particulate concentration in the processed flue gas at the pilot plant was about 7 gm/dscm which is typical of many coal-fired applications.
- No significant change in particulate composition was measured across the SFGT reactor.
- The concentrations of both CO and HC's were reduced across the SFGT reactor. It is believed this reduction was due to oxidation.
- The maximum potential emission rates of HCN and Nitrosoamines from the SFGT process are well below the levels which are considered safe in terms of adverse health effects.
- The technique used for measuring N_2O proved unsatisfactory for the quantity of N_2O (if any) present in the flue gas at the pilot unit.

4.5 CONTINUOUS SO_2 AND NO_x MONITOR CERTIFICATION RESULTS

Certification tests were conducted for the SO_2 and NO_x monitors used to measure flue gas concentrations of pollutants at the inlet and outlet of the reactor. These tests were included in the independent evaluation program to insure the quality of the pilot plant performance data being collected by UOP. As discussed earlier, the certification of continuous monitors involves a formal procedure developed by EPA to insure the accuracy of monitors used in determining a source's compliance with applicable NSPS. For the most part, these procedures were followed in conducting the tests at the SFGT pilot plant. However, due to the nature of the pilot plant operation (experimental rather than a compliance unit) some modifications were made to the certification test procedures (see Section 3.4.3).

Table 4-14 summarizes the results of the continuous monitor certification tests while Appendix C contains more details of the test results. As shown in Table 4-14, the test results for both the NO_x and SO_2 continuous monitors met the performance specifications with one exception; the relative accuracy of the outlet NO_x monitor was over 50 percent while the performance specifications require a relative accuracy of 20 percent or less. These data indicate that with the exception of the outlet NO_x analyzer, the continuous monitors were making accurate measurements of flue gas NO_x and SO_2 concentrations. It should be noted that 24-hour zero and calibration tests were not included in the certification tests since the instruments were calibrated at least every two hours, thus making the 24-hour drift tests meaningless. In addition, only one SO_2 monitor was used, so, with the exception of response time and relative accuracy, the inlet and outlet SO_2 monitor test rests are identical.

TABLE 4-14. RESULTS OF THE CONTINUOUS MONITOR CERTIFICATION TESTS AT THE SFGT PILOT PLANT

Certification Test	Performance Specification	Inlet SO_2[1] Monitor	Outlet SO_2[1] Monitor	Inlet NO_x Monitor	Outlet NO_x Monitor
Calibration error					
-high level	$\le$5%	1.4	1.4	3.85	2.52
-mid level	$\le$5%	0.7	0.7	4.62	2.62
Response time	$\le$15 min	0.8	1.3	1.7	0.8
Zero drift (2 hour)	$\le$2%	0.25	0.25	0.64	1.04
Calibration drift (2 hour)	$\le$2%	0.49	0.49	1.35	1.18
Relative accuracy	$\le$20%[2]	14.0	8.6	12.6	52.3

[1] One instrument was used to measure both inlet and outlet of the reactor.
[2] Alternatively, $\le$10 percent of the applicable emissions standard.

The poor relative accuracy of the outlet NO_x analyzer shown in Table 4-14 would tend to indicate that the monitor was making inaccurate measurements of flue gas NO_x concentrations. However, there are several factors which must be considered when evaluating these test results. First, the absolute error in the Method 7 versus the monitor measurements was only 16 ppm on the average. This is a relatively small difference. A second factor, which indicates that the outlet NO_x monitors performance was within acceptable limits, is that the performance specifications require the relative accuracy be less than or equal to 20 percent or 10 percent of the applicable standard, whichever is greater. Use of the standard as a basis for relative accuracy calculations is in recognition of the inaccuracy of the Method 7 analysis at low levels. For example, using the NSPS for bituminous coal-fired sources as a basis, the relative accuracy of the outlet NO_x monitor is approximately 5 percent of the applicable standard, which is within acceptable limits. Because the relative accuracy of the outlet NO_x monitor was within 10 percent of the applicable standard, it was determined that the outlet NO_x monitor was performing acceptably.

Overall, the results of the certification tests indicate that the continuous NO_x and SO_2 monitors at the SFGT pilot unit were performing acceptably. Therefore, the NO_x and SO_2 concentration data collected during the pilot plant tests by UOP are representative of the pilot plant's performance. This is especially true in light of UOP's extensive monitor maintenance program which was designed to insure the accuracy and quality of the performance data collected.

SECTION 5

EVALUATION OF THE SFGT PROCESS

The overall objective of this study was to determine the technical and economic feasibility of applying the SFGT process to a coal-fired utility boiler based on the results of the pilot plant tests. The approach used to meet this objective consisted of several elements. First, a basis was defined to permit preparation of a conceptual design and completion of material and energy balances for a specific application of the SFGT process. The basis is a 500 MW coal-fired boiler and is identical to that used by TVA in preparing a preliminary economic analysis of several flue gas treatment processes including the SFGT process. The basis identified material flows to the process, required reductions in NO_x and SO_2 emissions, and performance characteristics of unit operations not examined during the pilot plant tests (e.g., the performance of the regeneration off-gas treatment facilities). Using this information in conjunction with the pilot plant test results, a conceptual design was prepared.

Material and energy balances were completed for the process using the conceptual design results and process data which are representative of the pilot plant's operation. The results of the stack sampling tests conducted by Radian were also considered in preparing the material and energy balances. The results of this work identified the raw material and energy requirements of the process for the 500 MW application. Finally, a cost estimate was prepared for an SFGT process applied to a 500 MW coal-fired boiler. This cost estimate used the estimate prepared by TVA as a basis. Equipment costs were adjusted for changes in process stream flowrates or other significant factors (e.g., changes in required acceptor volume). Using adjusted equipment costs and the calculated raw material and energy requirements, TVA's estimate was modified and a new cost estimate developed.

This section presents a discussion of the elements which comprised the evaluation of the SFGT process. The basis for the evaluation is defined and the philosophy used in preparing the conceptual design is discussed. The conceptual design results are presented along with details and results of the material and energy balance calculations. This includes a quantative analysis of the heat credits associated with the 500 MW application of the SFGT process. The results of the cost estimate are also presented with details of how the estimate was prepared. Finally, a summary of results is presented with a discussion of how the results impact the technical and economic feasibility of the SFGT process.

5.1 BASIS FOR THE EVALUATION OF THE SFGT PROCESS

This evaluation of the SFGT process consisted of examining the raw material and energy requirements and capital and annualized costs of the SFGT process for a specific application. This form was chosen for the evaluation to provide a basis for comparing the costs of the SFGT process to the costs of other SCR processes which have been evaluated by TVA. In order to make these comparisons meaningful, it was necessary to use the same basis in this evaluation as was used by TVA in preparing their preliminary economic analysis. TVA's design basis is presented in detail in a report entitled "Preliminary Economic Analysis of NO_x Flue Gas Treatment Processes" (EPA-600/8-80-021).[1] The following discussion summarizes the aspects of the design basis which are applicable to this evaluation of the SFGT process.

Power Plant Characteristics

Only one power plant was used in preparing the evaluation of the SFGT process. This is a new, 500 MW coal-fired boiler, with an assumed Midwestern location for purposes of preparing cost estimates. The fuel for the plant was a coal having a heating value of 5820 kcal/kg and containing 3.5 percent sulfur and 16 percent ash. The coal composition and the input coal requirements (based on a heat rate of 2.27 Mcal/kWh) for the 500-MW boiler are listed in Table 5-1.

TABLE 5-1. BASE CASE COAL COMPOSITION AND INPUT FLOW RATE
(500-MW new unit, 2.27 Mcal/kWh heat rate)

Component	Wt %, as fired	kg/hr
C	57.56	111,950
H_2	4.14	8,030
N_2	1.29	2,490
O_2	7.00	13,610
S	3.12	6,080
Cl	0.15	270
Ash	16.00	31,120
H_2O	10.74	20,870
Total	100.00	194,420

The composition of the flue gas at the exit of the economizer is that which will be processed by the SFGT process since the temperature required in the reactor is close to the economizer exit temperature. This flue gas composition is presented in Table 5-2 and was estimated based on the assumption that 95 percent of the sulfur in the coal is emitted in the flue gas as SO_x with 99 percent as SO_2 and 1 percent as SO_3. It is also assumed that 80 percent of the ash is emitted with the flue gas stream. The NO_x concentration of the flue gas was estimated to be 640 ppm and consists of approximately 95 percent nitric oxide (NO) and 5 percent nitrogen dioxide (NO_2).

TABLE 5-2. FLUE GAS COMPOSITION AND FLOW RATE AT THE ECONOMIZER OUTLET (2.27 Mcal/kWh, 500-MW new unit, coal-fired, 3.5% S, 5820 kcal/kg HHV as fired, at 375°C)

Component	Vol %	kg/hr
N_2	73.39	1,412,000
O_2	3.23	71,000
CO_2	13.56	410,100
SO_2	0.26	11,400
SO_3	0.003	144
NO_x	0.064	1,365
HCl	0.012	300
H_2O	9.48	117,300
Total	100.00	2,023,600

Emission Reduction Requirements

Although the pre-1979 new source performance standards (NSPS) for new, coal-fired utility boilers were expressed on a mass emissions per unit heat input basis, the 1977 amendments to the Clean Air Act of 1970 required establishment of NSPS that specify a percent reduction as well as a maximum emission rate with respect to SO_2. This was accomplished in the 1979 NSPS. Therefore, the SFGT process included in this evaluation was designed based on a reduction efficiency of 90 percent for both NO_x and SO_2 emissions. This level of emission reductions is equal to that required by the 1979 NSPS for SO_2 but it is above NSPS levels for NO_x. The level of NO_x reduction required in this evaluation was selected to determine the cost of achieving 90 percent NO_x reduction using SCR.

SFGT System Design Characteristics

Using the information presented in the preceding discussion as a basis, it is possible to prepare a design of an SFGT process which will meet the emission reduction requirements. However, this design could take many forms without some additional restrictions. Some of the specific characteristics of the

SFGT process design which were used by TVA and incorporated in this evaluation are presented in Table 5-3. It must be emphasized that the system characteristics shown in Table 5-3 are options which would be selected based on economic considerations of a particular application. The options selected by TVA do, however, represent those which might be expected in a typical utility application.

TABLE 5-3. CHARACTERISTICS OF THE SFGT PROCESS SELECTED FOR EVALUATION PURPOSES

System Characteristic	Option Selected
• Number of Reactors	• 8 Reactors total - 6 process flue gas while 2 are regenerated.
• Reducing Gas Used	• Hydrogen.
• Reducing Gas Source	• Steam Naphtha Reformer.
• Regeneration off-gas handling	• Gas compression and storage for flow smoothing to SO_2 processing plant.
• SO_2 Processing	• The concentrated SO_2 stream produced by the SFGT process is sent to a contact sulfuric acid plant.

Another option included in this evaluation, but not shown in the table, is the use of an open recycle arrangement which permits virtually infinite turndown of the SFGT process. The open recycle arrangement is shown schematically in Figure 5-1. As illustrated, open ductwork connects the outlet of the reactor with the suction side of a fan required to overcome the reactor pressure drop. As load and flue gas flowrate decline, flue gas is recycled from the outlet to the inlet of the reactor. This results in good turndown characteristics for the process. Since gas velocities in the reactor remain constant, even at low loads, this maintains a high rate for the SO_2 and NO_x removal reactions which, as discussed in Section 4, decrease with decreasing gas velocities.

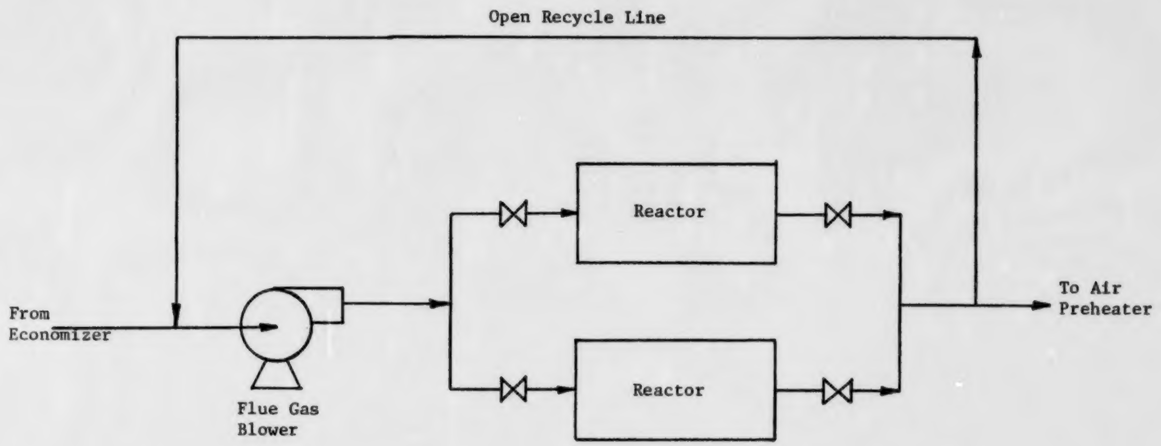
Open Recycle Line
From
Economizer
Flue Gas
Blower
Reactor
Reactor
To Air
Preheater

Figure 5-1. Schematic of open recycle arrangement with the SFGT process.

5.2 CONCEPTUAL DESIGN OF THE SFGT PROCESS FOR A 500 MW COAL-FIRED BOILER

The first step in the evaluation of the SFGT process was to prepare a conceptual design for a 500 MW application of the process using the results of the pilot plant tests to define key process operating parameter and performance levels. In order to complete this step, it was necessary to evaluate and reduce the pilot plant test results to a form which would serve as a basis for the design. It was also necessary to make judgements concerning extrapolation of results from the pilot plant to a 500 MW scale.

With the pilot plant data in the appropriate form, it was then possible to define levels of key operating parameters such as the NH_3/NO_x injection ratio, flue gas space velocity, reactor operating temperature, etc. It was also possible to determine the quantity and configuration of acceptor required to reduce both NO_x and SO_2 emissions by 90 percent for a 500 MW application. Once these items were defined, the conceptual design was essentially complete and material and energy balance calculations could be made based on the conceptual design results.

The following discussion presents the results of the conceptual design. It includes details of how the pilot plant test data were reduced and how those data were interpreted. It also includes a discussion of the general philosophy followed in preparing the design along with specific details of how the design was prepared.

5.2.1 Philosophy Used to Prepare the Conceptual Design

UOP conducted a large number of tests with the SFGT pilot plant. These tests were conducted under a variety of conditions using three separate charges of acceptor material. For purposes of this evaluation it was necessary to determine how these test results would be interpreted to quantify process performance and, in fact, which test results would be used to prepare the conceptual design. The general philosophy followed in evaluating test data and in preparing the conceptual design for a 500 MW plant was to use only those techniques and operating conditions which had been well documented in the pilot plant tests. In some cases it was necessary to extrapolate the test results, but this was minimized. The following discussion presents specific details of which tests were selected as a basis for this evaluation.

Several factors were considered in selecting the tests whose results would be used as a basis for this evaluation. First, it was considered desirable to have a large number of tests with repeatable results as a basis. The principal reason for this was that a greater number of tests results in a more accurate characterization of the processes performance and more accurate estimates of process operating parameters such as reactor pressure drop, hydrogen consumption, NH_3/NO_x injection ratio, etc. Second, it was considered desirable to use tests with operating conditions similar to those in which Radian conducted the secondary emissions sampling program. For these reasons it was decided to use selected results of the NO_x/SO_2 demonstration test conducted during June 1980.

The NO_x/SO_x demonstration test consisted of approximately 180 cycles conducted under essentially identical conditions. This provided an accurate charactization of key process operating parameters associated with specific levels of process performance. It was also during these tests that Radian conducted the majority of the quality assurance and secondary emissions sampling tests so those results are directly applicable to a conceptual design based on the demonstration tests.

As mentioned earlier, the general philosophy in preparing the conceptual design was to use the pilot plant data to the maximum extent and limit any extrapolation of results. More specifically, the design levels of key process operating parameters such as temperature and flowrate were based strictly on the levels measured during the NO_x/SO_2 demonstration tests even though the optimization tests indicated it might be possible to improve process performance by changing some process operating parameters. Since process performance at other process operating parameter levels was not accurately characterized, it was not possible to quantitively account for the effects of such changes.

The same philosophy was followed in defining process operation for the conceptual design. The conceptual design was limited to the mode of process operation employed during the NO_x/SO_2 demonstration tests even though modification of process operation (e.g. the use of a preoxidation and cooling step) indicated potential for improvements in process performance. It was necessary to make some changes in the conceptual design as compared to the pilot plant, but every effort was made to minimize such changes. Where differences between pilot plant operation and the conceptual design do exist, they are discussed in detail in the following section.

5.2.2 Pilot Plant Data Used to Prepare the Conceptual Design

The pilot plant data used to prepare the conceptual design were from the NO_x/SO_2 demonstration test. Because of the large number of cycles which comprised this demonstration test, it was possible to accurately characterize the average value of key process operating parameters during an acceptance or regeneration period. The repeatability of the test results is evidenced by the narrow range of the 95 percent confidence intervals for the key process operating parameters which were presented in Table 4-10.

Unfortunately, these data alone were not sufficient to characterize the performance of the SFGT process for the conceptual design. In addition, information on the performance of the process as a function of time during an acceptance period was needed. It was necessary to develop representative "slip" curves which quantify NO_x and SO_2 concentrations at the reactor outlet as a function of time. These representative slip curves were then used in conjunction with the other process data from the NO_x/SO_2 demonstration test to prepare the conceptual design.

The following discussion presents details of how the representative slip curves were developed and interpreted and how the conceptual design was prepared.

Development of Representative Slip Curves

Because of the number of cycles included in the NO_x/SO_2 demonstration test, it was not practical to prepare a slip curve which represented an average for the entire test. Instead, representative slip curves were developed based on selected cycles during the demonstration test. These cycles were selected such that the average level of their process operating parameters was close to the average level for the entire demonstration test.

A total of 12 cycles were selected for developing the representative slip curves. Strip charts which recorded outlet NO_x and SO_2 concentrations were digitized and a slip curve representing the average of the 12 cycles was produced along with upper and lower 95 percent confidence intervals for the slip curves. These curves, which were presented in Section 4.2, served as a basis for the conceptual design.

Interpretation of the Representative Slip Curves

The representative slip curves show the concentrations of NO_x and SO_2 at the reactor outlet as a function of time. In order to use these data as the basis for the conceptual design it was necessary to modify the slip curves and interpret how they changed with changes in design parameters. The following discussion presents the methodology used to interpret the representative slip curves and identifies any assumptions which were made in the interpretation. Because of the differences in the factors which control NO_x reduction and SO_2 removal, the interpretation of these slip curves is discussed separately.

SO_2 Slip Curve--

The first step in interpreting the SO_2 slip curve was to convert it to a general form giving SO_2 removal as a function of time. This was done by fitting an equation to the representative slip curve and using this equation to predict SO_2 removal as a function of time. These relationships are shown in Equations 5-1 and 5-2.

$SO_{2_{out}} = f(t)$ (5-1)

$$SR_I = 1 - \frac{SO_2out}{SO_2in} = 1 - \frac{f(t)}{SO_2in} \quad (5\text{-}2)$$

where $SO_{2_{in}}$ = inlet SO_2 concentration

$SO_{2_{out}}$ = outlet SO_2 concentration

SR_I = instantaneous SO_2 removal efficiency

t = acceptance time

Using Equation 5-2 it was then possible to predict the time averaged SO_2 removal as a function of inlet SO_2 concentration and acceptance time. It was assumed that for a 7-meter reactor, the instantaneous SO_2 removal efficiency is a function of the quantity of copper oxide in the reactor for constant conditions of flowrate and temperature. With this assumption, the SO_2 removal rate was then defined by Equation 5-3.

$$SR_I = g(CuO) \quad (5\text{-}3)$$

The relationship between f(t) and g(CuO) is somewhat complex. In order to define this relationship the copper oxide concentration must be determined as a function of time as shown below.

$$CuO(t) = CuO_I - C\int_o^t SR_I dt \quad (5\text{-}4a)$$

$$= CuO_I - C\int_o^t (1- \frac{f(t)}{SO_{2_{in}}})dt \quad (5\text{-}4b)$$

$$= CuO_I - (C)(t)(SR_A) \quad (5\text{-}4c)$$

where CuO(t) = the quantity of copper oxide as a function of time during an acceptance period

CuO_I = the quantity of copper oxide in the reactor at the start of an acceptance period

C = the average molar flowrate of SO_2 into the reactor during the acceptance period. This number was based on the average for the 12 cycles used to prepare the representative slip curve.

SR_A = the time averaged SO_2 removal during an acceptance period.

The integral in Equation 5-4 represents the product of the time averaged SO_2 removal and the acceptance time. When multiplied by the molar flowrate of SO_2 to the reactor (C), this equals the quantity of $CuSO_4$ formed during an acceptance period of length t.

Equation 5-4 can be solved for time as a function of copper oxide concentration as represented by Equation 5-5.

$$t = h(CuO) \qquad (5\text{-}5)$$

This expression for time can then be substituted into Equation 5-2 which results in instantaneous SO_2 removal being expressed as a function of the quantity of CuO in the reactor (Equation 5-3). Using Equation 5-3 it was then possible to determine the time averaged SO_2 removal efficiency as a function of varying acceptance times and SO_2 concentrations.

For given levels of copper oxide at the start and completion of an acceptance period, the time averaged SO_2 removal is expressed by Equation 5-6.

$$SR_A = \left[\int_{CuO_I}^{CuO_F} g(CuO)\,d(CuO)\right] \div (CuO_F - CuO_I) \qquad (5\text{-}6)$$

where CuO_F = quantity of CuO at the end of acceptance

With SR_A defined, the relationship between acceptance time, time averaged SO_2 removal, and inlet SO_2 concentration can be used to calculate one of the three if two are specified. This relationship is shown in Equation 5-7.

$$CuO_F - CuO_I = (SO_{2\,in})\,(SR_A)\,(t)\,(F) \qquad (5\text{-}7)$$

Where: Cu_F and Cu_I are expressed as gram moles,

$SO_{2\,in}$ as ppm,

t as min, and

F = molar flowrate of flue gas to the reactor (gram moles/min)

For a given quantity of copper oxide at the start of acceptance, the acceptance time and inlet SO_2 concentrations can be specified and the resultant removal calculated. Alternatively, removal and one other variable can be specified and the undefined variable calculated.

The relationships presented in Equations 5-6 and 5-7 form the basis of the conceptual design. When used in conjunction with the representative NO_x slip curve, it is possible to define system design parameters such that a specific level of NO_x reduction and SO_2 removal can be achieved simultaneously.

NO_x Slip Curve--

Interpretation of the NO_x slip curve required that the instantaneous NO_x reduction efficiency be expressed as a function of time. Again this was done by fitting an equation to the representative slip curve and transforming it as shown in Equations 5-8 and 5-9.

$$NO_{x\,out} = f(t) \qquad (5\text{-}8)$$

$$\text{Instantaneous } NO_x \text{ reduction} = NR_I = 1 - \frac{f(t)}{NO_{x\,in}} \qquad (5\text{-}9)$$

Initially it was thought that NO_x slip would be a function of the relative amounts of copper oxide and copper sulfate in the reactor since these are the compounds which catalyze the NO_x reduction reactions. However, the results of the preoxidation and cooling tests indicated that the quantity of copper sulfate required for the NO_x reduction reactions to reach the steady state level is present shortly after the start of an acceptance period. As discussed in

Section 4, the factor which appears to limit the rate of NO_x reduction is the temperature of the reactor internals, which depends on the rate of heat transfer from the acceptor and internals to the flue gas. For constant conditions of inlet temperature and flowrate, the heat transfer rate and thus, the NO_x reduction efficiency are functions of time.

Once the NO_x reduction efficiency had been determined to be a function of time for constant operating conditions, the time averaged NO_x reduction could easily be defined for any given acceptance time. This relationship is illustrated by Equation 5-10.

$$\text{Time averaged } NO_x \text{ reduction} = NR_A = \int_o^t \left(1 - \frac{f(t)}{NO_{x\,in}}\right) dt \qquad (5\text{-}10)$$

Using this equation in combination with Equations 5-6 and 5-7 permitted sizing an SFGT reactor for specified levels of NO_x reduction and SO_2 removal.

Since NO_x reduction is a function of time for constant conditions of reactor inlet temperature and flue gas flowrate, the sizing of the reactor becomes a relatively straightforward problem. However, some restrictions on the pilot plant operation make the use of the NO_x reduction vs time curve unrepresentative of potential full-scale operation. For this reason it was decided to develop a NO_x reduction vs time relationship for higher NH_3/NO_x injection ratios and for reactors with bed depths greater than 7 meters. This was done for both these variables by developing NO_x reduction curves which were "parallel" to the original representative slip curve.

The relationship between NO_x reduction and the NH_3/NO_x injection ratio was well defined by the steady state NO_x tests (see Figure 4-7). This relationship was used to define a parallel NO_x slip curve at varying NH_3/NO_x injection ratios. For a new NH_3/NO_x injection ratio, the distance between the parallel curves was determined to be equal to difference between the NO_x reduction efficiency at the original NH_3/NO_x ratio and the NO_x reduction efficiency at the new NH_3/NO_x injection ratio. The NO_x reduction efficiencies at the two NH_3/NO_x injection ratios were those defined by Figure 4-7.

Changes in reactor depth were also used to define parallel NO_x reduction vs time curves. The increment between two curves due to a change in reactor depth was determined based on the assumption that instantaneous NO_x reduction efficiency is first order with respect to concentration. This indicates that if, for example, a seven meter reactor has a steady state NO_x reduction efficiency of 90 percent, then an additional seven meters of reactor depth would reduce the remaining NO_x by 90 percent for a total of 99 percent NO_x reduction at steady state. Mathematically, this relationship is expressed by Equation 5-11.

$$NR_I = I-ae^{bD} \tag{5-11}$$

Where: a and b are empirical constants

D = reactor depth

Using this relationship and the steady state NO_x reduction efficiency from the representative slip curve, a and b were determined. Then Equation 5-11 was used to estimate steady state NO_x reduction at reactor depths of 8 and 9 meters. The change between steady state NO_x reduction at the various reactor depths was used to define parallel NO_x reduction vs time curves for 8 and 9 meter reaction depth.

In preparing the conceptual design, a reactor depth of 9 meters was ultimately used and an NH_3/NO_x injection ratio of 1.5 was assumed. The resultant parallel NO_x reduction vs. time curve is presented in Figure 5-2, where it is compared with the NO_x reduction vs. time curve based on the pilot plant test data. The curves are not completely parallel but rather, are identical during the initial stages of acceptance. As shown, after about 7 minutes, when the oxidation wave has passed through the reactor, the curves begin to separate and are completely parallel 25 minutes into acceptance.

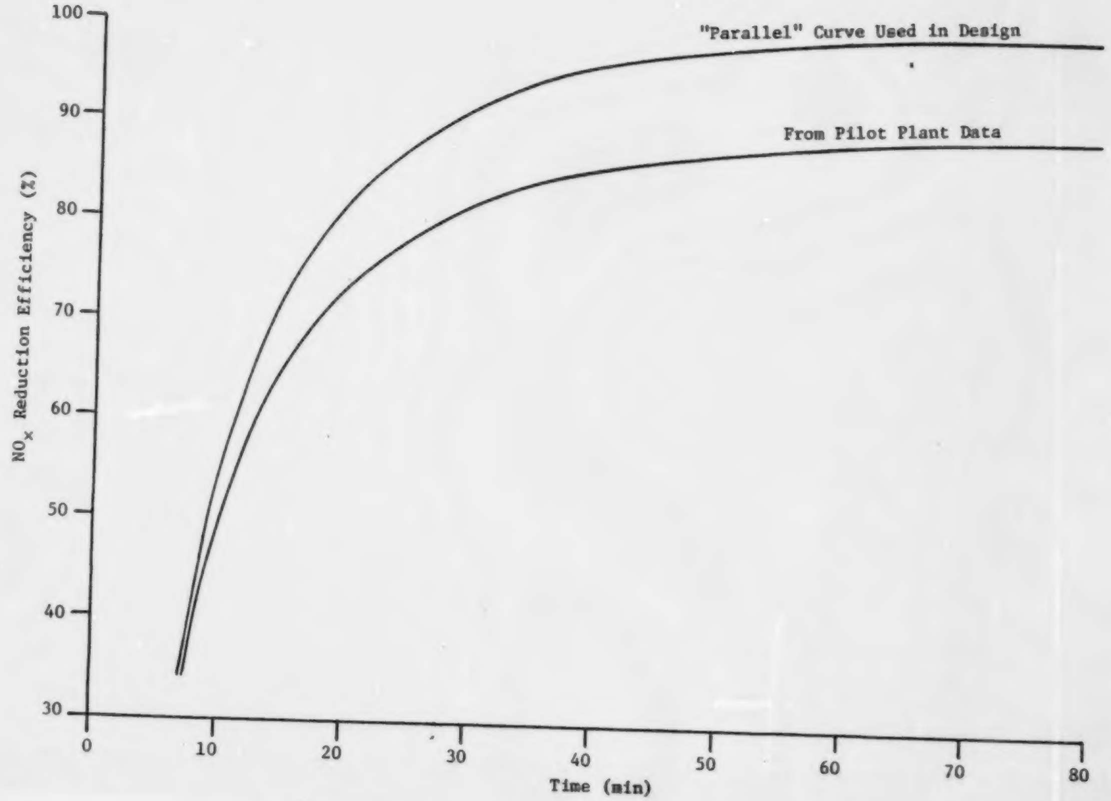

Figure 5-2. NO_x reduction vs. time used in preparing the conceptual design.

The parallel NO_x reduction curve was developed based on engineering judgement and it should be noted that it may not represent actual process performance under the design conditions. However, the differences in the design which result from the modified NO_x reduction vs time curve are not significant in terms of their impact on the process costs presented later in this report. The modified curve does result in a reduction of estimated costs but this reduction appears realistic.

5.2.3 Conceptual Design Limitations and Procedures

Some of the techniques used to prepare the conceptual design of the SFGT process were discussed above. This section summarizes the limitations which served as the basis for the conceptual design and the procedure followed in preparing the design.

Design Limitations

Table 5-4 presents limitations which were used in conjunction with TVA's basis and the pilot plant data to develop a conceptual design of a 500 MW SFGT process application. The required emission control efficiencies shown in Table 5-4 are from TVA's basis. The limitations on each of the other variables are discussed below.

TABLE 5-4. LIMITATIONS OF THE SFGT CONCEPTUAL DESIGN

Parameter	Level
NO_x Reduction efficiency	90 percent
SO_2 Removal efficiency	90 percent
Flue gas flowrate	1600 Nm^3/hr/unit cell of crossection
Flue gas/reactor inlet temperature	400°C
NH_3 injection delay	0 min
Fraction of acceptor regenerated	100 percent
Acceptance time	As required to meet emission levels
Reactor depth	As required to meet emission levels
NH_3/NO_x injection ratio	1.5 maximum

Temperature--

Flue gas temperature at the reactor inlet is required to be 400°C. This requirement is based on the fact that data used to develop the representative slip curve and the data collected during the NO_x/SO_2 demonstration test are for flue gas temperatures of approximately 400°C. Also, the optimization tests conducted by UOP determined that flue gas temperatures can have a significant impact on NO_x and SO_2 reduction efficiencies. However, the effect of temperature was not well quantified.

The requirement for a fixed temperature at the reactor inlet obviously results in a requirement for some form of control system which varies the quantity of heat extracted from the flue gas in the economizer. In preparing the design and subsequent cost estimate it was assumed that such a control system is commercially available and does not add significantly to the capital costs of the process.

Flowrate--

Flue gas flowrate per unit cell of reactor crossection was required to be 1600 Nm^3/hr. This requirement was based on the fact that a flowrate of 1600 Nm^3/hr was representative of the NO_x/SO_2 demonstration test. As a consequence the representative slip curves are only valid for this particular flowrate. At other flowrates, SO_2 and NO_x reaction rates change with consequent changes in the slip curves. Unfortunately, not enough tests were conducted to quantify the change well enough to permit the use of flowrate as a design variable.

NH_3 Injection Delay--

During the NO_x/SO_2 demonstration test, no NH_3 injection delay was used. In addition, the results of the NH_3 injection delay tests indicated that no significant benefit resulted from its use. As a consequence no NH_3 injection delay was considered in the conceptual design.

Fraction of Acceptor Regenerated--

The fraction of acceptor regenerated in the conceptual design was assumed to be identical to the fraction regenerated during the NO_x/SO_2 demonstration tests. This fraction should be close to 100 percent due to the way the regeneration step was monitored in the pilot plant tests. UOP used a time of flight-mass spectrometer to monitor H_2 and SO_2 in the regeneration off gas. Using this instrument as a guide, regeneration was terminated when the SO_2 concentration in the off gas began to decline and the H_2 concentration in the off gas began to increase. Due to the nature of the regeneration reaction kinetics, significant H_2 breakthrough should only occur after the bed is completely regenerated.

NH_3/NO_x Injection Ratio--

The NH_3/NO_x injection ratio was limited to a maximum of 1.5 for several reasons. First, this ratio represents the upper limits of the NH_3/NO_x ratio tests conducted during the NO_x-only demonstration test and thus the upper limit of the pilot plant data. As discussed earlier, the test results from the NO_x-only demonstration test were used to develop "parallel" NO_x slip curves at varying NH_3/NO_x injection ratios. A second reason for limiting the NH_3/NO_x injection ratio to 1.5 was that extrapolation of the NO_x-only test results to higher NH_3/NO_x injection ratios indicate that little improvement in NO_x reduction efficiency would be expected while NH_3 emissions would increase significantly.

Reactor Depth and Acceptance Time--

These two parameters were considered design variables in preparing the conceptual design and their final levels will be discussed in the following section. Originally the reactor depth was limited to 7 meters since this was the basis for the representative slip curves. However, after the first design iteration it seemed reasonable to extend the reactor depth. This resulted in a slight decrease in capital and operating costs for the conceptual design.

Conceptual Design Procedures

Once limitations were placed on process operating parameters it was possible to proceed with preparation of the conceptual design. The procedure which was followed involved the use of mathematical relationships which have been developed in this section and are summarized in Table 5-5.

TABLE 5-5. RELATIONSHIPS USED TO PREPARE THE CONCEPTUAL DESIGN

Relationship	Equation No.
$SR_A = \left[\int_{CuO_I}^{CuO_F} g(CuO)d(CuO) \right] \div (CuO_F - CuO_I)$	(5-6)
$(CuO_F - CuO_I) = (SO_{2_{in}})(SR_A)(t)(F)$	(5-7)
$NR_A = \left[\int_o^t (1 - \frac{f(t)}{NO_{x_{in}}})dt \right] \div t$	(5-8)

The first step in evaluating the equations shown in Table 5-5 was to specify the reactor bed depth and consequently the quantity of copper oxide present at the start of an acceptance period (i.e., CuO_I). Once the reactor depth was set, it determined which of several possible parallel NO_x slip curves would be used (i.e., which of several expressions for instantaneous NO_x removal as a function of time would be substituted into Equation 5-8). Equation 5-8 was solved for the acceptance time which resulted in 90 percent NO_x reduction. Equation 5-6 was then solved to determine the value of CuO_F which resulted in 90 percent SO_2 removal. With values for CuO_F and t, Equation 5-7 was solved to determine the inlet SO concentration which would result in 90 percent SO_2 removal at the same acceptance time required to achieve 90 percent NO_x reduction.

One iteration through this procedure resulted in one potential conceptual design for the SFGT process. But the results required that SO_2 concentration at the reactor inlet be considered as a design variable. For most flue gas desulfurization systems, the use of inlet SO_2 concentration as a design variable is not possible. However, the unique nature of the SFGT process permits the SO_2 concentration at the reactor inlet to be varied by recycling treated flue gas from the reactor outlet. Of course, the use of recycle requires that the reactor have a crossection which increases in proportion to the recycle rate.

As discussed earlier, it was originally intended to restrict the depth of the reactor to a maximum of seven meters. However, this resulted in a recycle rate which was a significant fraction of the total flue gas flowrate through the reactor. Therefore, it was decided to increase the reactor depth and thus decrease the recycle rate. This necessitated making several assumptions concerning the NO_x and SO_2 slip curves at increased reactor depths. One assumption made involved the development of parallel NO_x slip curves which would serve as a basis for calculating NO_x reduction efficiency at varying reactor bed depths. The second assumption made was that the relationship between instantaneous SO_2 removal efficiency and the quantity of copper oxide in the reactor would be unchanged at increased reactor depths. This permitted the use of Equation 5-6 at varying reactor depths.

While there may be some uncertainty in making both these assumptions, their net effect on the conceptual design results was not significant. They did result in the requirement for less acceptor material and a lower overall reactor pressure drop. This resulted in somewhat lower capital and operating costs for the 500 MW application of the SFGT process.

5.2.4 Conceptual Design Results

The preceding discussion has summarized the data used and the procedures employed in preparing the conceptual design of the SFGT process. The discussion which follows summarizes the results of the design calculations and some additional calculations required to complete the design. This discussion does not cover details of the material and energy balance calculations which are discussed in subsequent sections of this report.

Table 5-6 summarizes the results of the conceptual design for a 500 MW application of an SFGT process. As shown, the key design variable levels are presented. These levels were determined based on the calculations outlined in the preceding discussion and on the basis defined in Section 5.1. These parameters and the design levels are discussed briefly below.

Acceptance Time

The acceptance time required for 90 percent NO_x reduction using a 9 meter reactor depth at an NH_3/NO_x injection ratio of 1.5 was determined to be 148 minutes. This value is based on the "parallel" NO_x slip curve which was presented in Figure 5-2. Integration of this curve from 0 to 148 minutes yields a time averaged NO_x reduction of 89.8 percent which is equivalent to an overall NO_x reduction efficiency of 90 percent considering the effects of flue gas recycle.

TABLE 5-6. RESULTS OF THE SFGT CONCEPTUAL DESIGN

Parameter	Design Level
Acceptance time (min)	148
Reactor depth (meters)	9
Inlet SO_2 concentration (ppm)	2548
Recycle rate (%)	1.8
NH_3/NO_x injection ratio	1.5
Overall NO_x/SO_2 reduction (%)	90
NO_x/SO_2 reduction across reactor (%)	89.8
Number of reactors	8
Crossectional area of each reactor (m^2)	40.75
Number of unit cells in each reactor	1467
SFGT system pressure drop (kPa)	3.93

Reactor Depth

The final reactor depth was determined to be 9 meters. This reactor depth yielded the required NO_x/SO_2 reduction efficiencies with a minimum of flue gas recycle. Compared to the 7 meter design case which required a recycle rate of 60 percent and an acceptance time of 160 minutes, the 9 meter design reduced the costs associated with this application of the SFGT process.

Inlet SO_2 Concentration and Recycle Rate

The inlet SO_2 concentration which results in 90 percent SO_2 removal at a reactor depth of 9 meters and an acceptance time of 148 minutes was determined to be 2548 ppm. This is slightly less than the SO_2 concentration of 2590 in the flue gas entering the reactor. The recycle rate required to reduce the inlet SO_2 concentration to 2548 was determined to be approximately 1.8 percent. This was estimated using Equation 5-12.

$$y = (2590 + 259x) \div (1 + x) \qquad (5\text{-}12)$$

where: x = the fraction of flue gas flow recycled

y = the required inlet SO_2 concentration = 2548 ppm

259 = the concentration of SO_2 in the flue gas exiting the reactor which, by definition = (2590) (0.1)

Overall and Actual NO_x/SO_2 Reduction Efficiencies

The overall NO_x and SO_2 reduction efficiencies were required to be 90 percent for the design of the SFGT process. However, the actual reduction efficiences across the reactor are somewhat less due to the recycle stream. The actual NO_x and SO_2 reduction efficiencies across the SFGT reactor are estimated to be 89.8 percent. With the recycle stream this results in NO_x and SO_2 concentrations at the reactor exit of 64 and 259 ppm respectively.

Reactor Configuration and Pressure Drop

The number of reactors required was not changed from the TVA design basis. There are a total of 8 reactors, 6 of which process flue gas while the remaining 2 are regenerated. The crossectional area of each reactor was determined based on total flue gas flow to the reactors in acceptance and the design limitation of 1600 Nm^3/hr per 0.25 m^2 of crossection. The total number of cells in each reactor equals the number in each reactor crossection times the reactor depth of 9 meters.

The reactor pressure drop was determined based on the pressure drop in the pilot unit and some assumptions for valves and associated ductwork. It was assumed that the ductwork, valves, gas distribution system, etc. had a total pressure drop of 1 kPa. It was also assumed that the reactor pressure drop increased linearly with the depth of the reactor. During the NO_x/SO_2 demonstration tests, the reactor pressure drop for a 7 meter bed was 2.28 kPa (see Table 4-10). Using this value results in an estimated pressure drop of 2.93 kPa for a 9 meter reactor and an overall pressure drop of 3.93 kPa for the SFGT process equipment.

5.3 MATERIAL BALANCE FOR A 500 MW SFGT PROCESS

The first step in completing the SFGT process evaluation was preparation of a conceptual design. Once this design was completed it was then possible to begin preparation material balance calculations which define raw material requirements for a 500 MW SFGT system. However, before the material balance could be completed, it was necessary to define the level of several process parameters including:

- H_2 required for regeneration,
- Steam required for regeneration,
- NH_3 emissions of the process; and
- SO_3 removal efficiency of the reactor.

Once these parameters had been defined, it was then possible to complete a material balance for a 500 MW SFGT system based on pilot plant data. The following discussion defines the parameters needed to complete the material balance and presents the results of the material balance calculations.

5.3.1 Process Parameters Needed to Complete the Material Balance Calculations

As discussed above, it was necessary to define several additional process parameters in order to complete the material balance calculations. These parameters affect the material balance calculations but do not impact the conceptual design results. The following discussion examines each of these parameters and defines their levels for use in the material balance calculations.

H_2 Required for Regeneration

The hydrogen requirements for the pilot unit were well characterized by the NO_x/SO_2 demonstration test, and these hydrogen requirements can be used to determine the H_2 requirements of the 500 MW SFGT system. However, the results of the pilot plant tests are not directly applicable to the full scale process. In order to determine the H_2 requirements for the full scale system, it is necessary to examine the pilot plant and conceptual design operating conditions and the reactions which result in H_2 consumption during regeneration.

During the NO_x/SO_2 demonstration test, the H_2/SO_2 molar feed ratio was approximately 4.21 (Table 4-10). Examination of the hydrogen slip curves indicates that approximately 4 percent of the total H_2 fed to the reactor slips through and exits with the regeneration off gas. Using 4 percent as representative of the H_2 slip, this indicates that the number of moles of H_2 which reacts is equal to 4.05 times the number of moles of SO_2 removed.

The reactions which consume hydrogen during regeneration are illustrated by Equations 5-13 and 5-14.

$CuSO_4 + 2H_2 \rightarrow Cu + 2H_2O + SO_2$ (5-13)

$CuO + H_2 \rightarrow Cu + H_2O$ (5-14)

During the demonstration test the average number of moles of SO_2 removed was approximately 161 which left 229 moles of CuO in the reactor. Using the stoichiometric coefficients from Equations 5-13 and 5-14, this indicates an H_2/SO_2 mole ratio of 3.42 which leaves approximately 100 gmols of H_2 unaccounted for.

Since no oxygen is present during the regeneration step, the unaccounted for H_2 must be due to consumption in some other reduction reaction. Several tests conducted by UOP over the year of pilot plant tests had indicated that a significant percentage of the copper on the acceptor was not being regenerated. It was believed that this was due to the formation of cupric sulfide (Cu_2S) via the reaction shown in Equation 5-15.

$2Cu + SO_2 + 2H_2 \rightarrow Cu_2S + 2H_2O$ (5-15)

Upon exposure to flue gas the Cu_2S would be expected to oxidize as illustrated by Equation 5-16.

$2\ Cu_2S + 5O_2 \rightarrow 2\ CuO + 2CuSO_4$ (5-16)

The $CuSO_4$ thus formed, would also have to be regenerated via the reaction shown in Equation 5-13. Therefore, each mole of Cu_2S formed results in the consumption of 3 moles of hydrogen in the regeneration step.

Several assumptions were made to estimate the H_2 consumption of the SFGT process for the 500 MW application. First it was assumed that the hydrogen which could not be accounted for during the pilot plant tests was consumed by Cu_2S formation. The second assumption made was that the fraction of copper on the acceptor which formed Cu_2S was constant for both the pilot plant and the 500 MW design. A third assumption made was that the H_2 slip would be the same for both the pilot plant and the full scale design (equal to 4 percent of total H_2 fed to the reactor). And finally, it was assumed that the H_2 purged from the reactors was proportional to the reactor volume. This resulted in an H_2/SO_2 mole ratio of 2.8 for the 500 MW material balance.

The H_2/SO_2 mole ratio of 2.8 does not include H_2 which must be vented when the reactor is being purged with steam before and after the regeneration step. The quantity was determined by assuming the purge step requires approximately 3 minutes of each 49.3 minute regeneration period. Assuming a constant H_2 flowrate throughout regeneration, the fraction of H_2 which must be vented is approximately 6 percent of the total flow from the steam-naphtha reformer. This results in an overall requirement of 2.97 moles of H_2 per mole of SO_2 removed from the flue gas.

Steam Required for Regeneration

The steam required to dilute the H_2 in the reducing gas for the 500 MW SFGT design was estimated based directly on the pilot plant data. The steam to hydrogen ratio during the NO_x/SO_2 demonstration test (from Table 4-10) averaged 4.04 moles steam per mole of H_2. For the H_2/SO_2 mole ratio of 2.8, this results in a steam requirement of 11.3 moles steam per mole of SO_2 removed by the process.

NH_3 Emissions From The Process

During the NO_x/SO_2 demonstration tests, NH_3 emissions were measured by both Radian and UOP. At an NH_3/NO_x injection ratio of 1.25, these emissions averaged approximately 15 ppm. NH_3 emissions were also measured during NO_x-only tests at the same NH_3/NO_x injection ratio and they averaged 49 ppm, about 3 times the emission rate during non-cyclic operation. The NH_3/NO_x injection ratio specified in the conceptual design is 1.5. Unfortunately, no tests were conducted at this injection ratio during cyclic operation so the NH_3 emissions could not be determined under these operating conditions.

However, tests were conducted at an NH_3/NO_x injection ratio of 1.5 during NO_x-only tests and NH_3 emissions were measured during these tests.

Assuming that the 3 to 1 ratio of NH_3 emissions during NO_x-only and cyclic operation is still valid at an NH_3/NO_x ratio of 1.5, then the NH_3 emissions for the conceptual design can be estimated. An additional assumption required is that NH_3 emissions are proportional to the inlet NO_x concentration. Based on the data presented in Figure 4-7 and the ratio of inlet NO_x concentration for the NO_x-only tests and for the conceptual design, the NH_3 emissions from the conceptual design were estimated to be 49 ppm. This value was used in preparing the material balance calculations for the 500 MW application of the SFGT process.

SO_3 Removed in the Reactor

As part of Radian's secondary emissions sampling program, the sulfur trioxide concentration of the flue gas was measured at the inlet and outlet of the reactor. The results of these tests indicated 99 percent removal of SO_3 in the reactor. While this figure is not significant from a material balance standpoint, it indicates this potential for additional heat recovery in the air preheater. As a result it can significantly affect the energy balance calculations. For both material and energy balance calculations, it was assumed that the reactor removes 90 percent of the incoming SO_3. This assumption was made as a conservative estimate since only two SO_3 measurements were completed during the secondary emissions sampling program.

5.3.2 Results of the Material Balance Calculations

With the required parameters defined, it was possible to complete a material balance for a 500 MW application of the SFGT process. This was done using TVA's material balance as a basis and the data generated during the pilot plant tests and secondary emissions sampling to modify that material balance. Where appropriate, ratios of modified stream flows to TVA's original flows were made to determine new flowrates (e.g., the quantity of air used to dilute/inject NH_3).

Figure 5-3 is a schematic of the SFGT process which indicates process streams and stream numbers used in preparing the material balance. This schematic and the stream numbers shown are consistent with those used by TVA. There are, however, two additional streams shown on Figure 5-3. These represent the flue gas recycle included in the design (Stream 45) and the hydrogen vented to the boiler during the period the reactor is purged (Stream 46).

The results of the material balance calculations based on the pilot plant data are summarized in Table 5-7. These represent the mass and volumetric flows to all significant pieces of process equipment in the 500 MW application of the SFGT process. These flowrates were estimated based on the data and assumptions outlined in the preceding discussion. The results of the material balance calculations serve as a basis for the energy balance calculations which are summarized in the following section. These flows also serve as a basis for estimating the size and consequent cost of process equipment for the 500 MW application of the SFGT process.

Table 5-8 summarizes the most significant results of the material balance calculations and compares those results with the material requirements identified by TVA in their preliminary economic analysis. As shown, steam and hydrogen requirements increase by approximately the same fraction. This indicates that the steam to H_2 ratio used in the TVA design is essentially identical to the ratio used during the pilot plant tests. The naphtha requirements increase in direct proportion to the hydrogen requirements. This is perhaps the single most important increase in a material flowrate since it has a significant impact on annual revenue requirements for this process. The NH_3 requirements increase significantly due to the high NH_3/NO_x ratio used in preparing the conceptual design. This reflects the relatively poor performance of the pilot plant at lower NH_3/NO_x injection ratios. Finally, the quantity of sulfuric acid is unchanged since the same quantity of SO_2 is being removed from the flue gas.

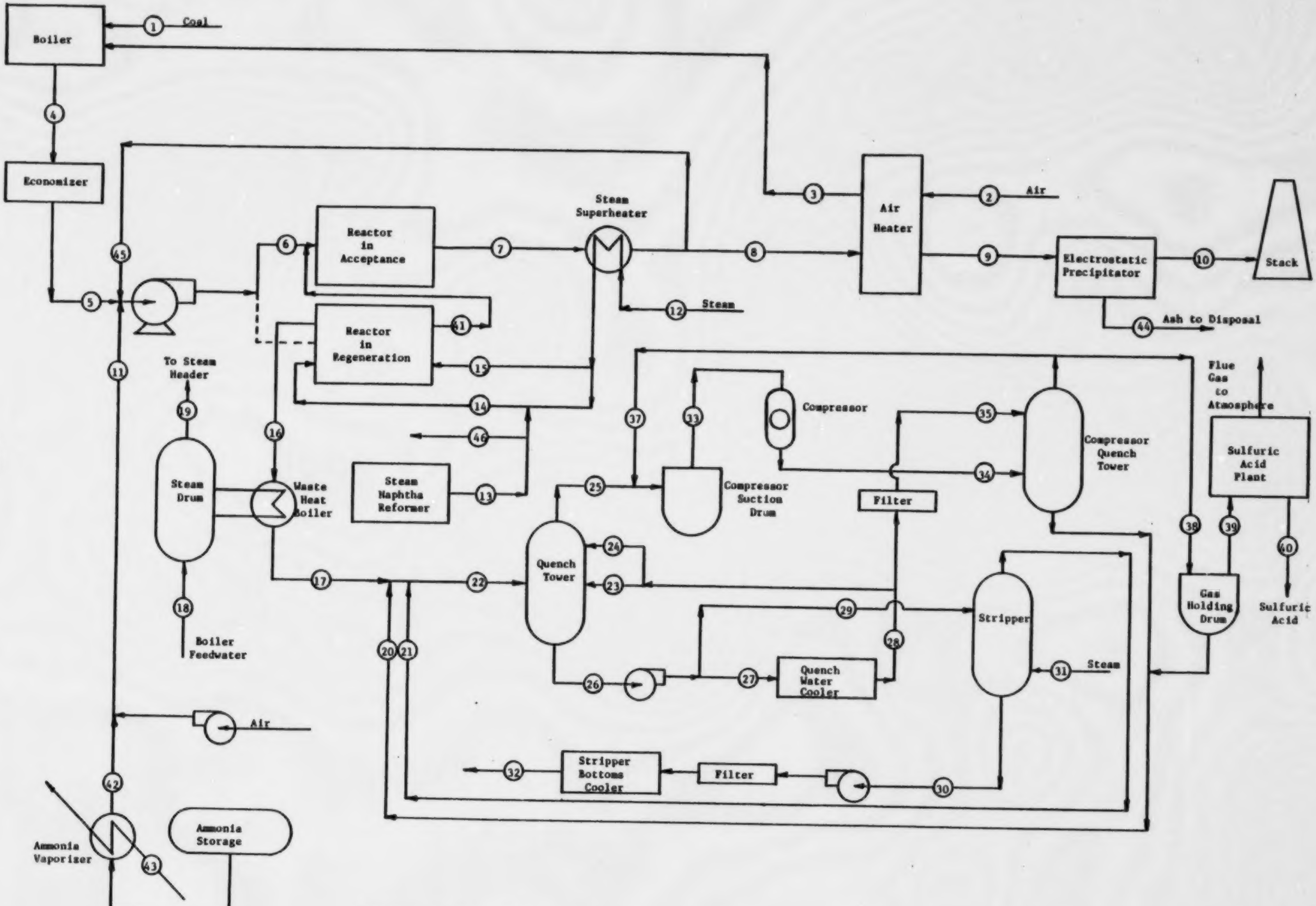
Boiler
1
Coal
4
Economizer
5
45
11
6
Reactor in Acceptance
7
Steam Superheater
8
3
Air Heater
2
Air
9
Electrostatic Precipitator
10
Stack
44
Ash to Disposal
12
Steam
Reactor in Regeneration
41
15
14
46
13
Steam Naphtha Reformer
16
Waste Heat Boiler
To Steam Header
19
Steam Drum
18
Boiler Feedwater
17
20
21
22
Quench Tower
24
23
25
26
37
33
Compressor
Compressor Suction Drum
35
34
Compressor Quench Tower
Filter
27
Quench Water Cooler
28
29
Stripper
31
Steam
30
Filter
Stripper Bottoms Cooler
32
38
39
Gas Holding Drum
Flue Gas to Atmosphere
Sulfuric Acid Plant
40
Sulfuric Acid
Air
42
Ammonia Vaporizer
43
Ammonia Storage

Figure 5-3. Schematic of a 500 MW application of the SFGT process.

TABLE 5-7. MATERIAL BALANCE FOR 500 MW SFGT SYSTEM*

Stream Number	1	2	3	4	5
Description	Coal to Boiler	Combustion Air to Air Pre-Heater	Combustion Air to Boiler	Flue Gas to Economizer	Flue Gas to Blower
Mass Flow (lb/hr)	428,600	4,546,200	4,101,800	4,516,100	4,516,100
Volume Flow (scfm)	-	1,005,000	906,700	957,000	957,000

Stream Number	6	7	8	9	10
Description	Flue Gas NH_3 Mixture to Reactor	Flue Gas to Steam Superheater	Flue Gas to Air Heater	Flue Gas to ESP	Flue Gas to Stack
Mass Flow (lb/hr)	4,680,200	4,658,300	4,576,300	5,020,700	4,965,700
Volume Flow (scfm)	992,900	993,500	976,000	1,074,200	1,074,200

Stream Number	11	12	13	14	15
Description	NH_3 Stream Injected Into Flue Gas	Steam to Steam Superheater	Hydrogen for Regeneration	Steam to Purge	Reducing Gas to Reactor
Mass Flow (lb/hr)	82,100	84,300	3,590	11,900	75,800
Volume Flow (scfm)	18,400	29,600	7,050	4,200	32,000

Continued/

*Note: For ease of comparison with TVA's results, the values in this table are presented in English units.

TABLE 5-7. (Continued)*

Stream Number	16	17	18	19	20
Description	Regeneration Off Gas to Waste Heat Boiler	Regeneration Off Gas to Quench Tower	Boiler Feed-Water to Steam Drum	Steam to Steam Header	Compressor Quench Tower Bottoms to Quench Tower
Mass Flow (lb/hr)	109,600	109,600	24,150	24,150	28,330
Volume Flow (scfm)	32,800	32,800	-	6,800	-

Stream Number	21	22	23	24	25
Description	Stripper Overhead to Quench Tower	Quench Tower Feed	Lower Quench Tower Recycle	Upper Quench Tower Recycle	Quench Tower Overhead
Mass Flow (lb/hr)	520	138,450	789,470	789,470	25,270
Volume Flow (scfm)	90	-	-	-	3,160

Stream Number	26	27	28	29	30
Description	Main Quench Tower Bottoms	Main Quench Bottoms to Cooler	Main Quench Bottoms from Cooler	Main Quench Bottoms to Stripper	Stripper Bottoms to Cooler
Mass Flow (lb/hr)	1,694,050	1,627,620	1,627,620	85,670	89,610
Volume Flow (scfm)	-	-	-	-	-

Continued/

*Note: For ease of comparison with TVA's results, the values in this table are presented in English units.

TABLE 5-7. (Continued)*

Stream Number	31	32	33	34	35
Description	Steam to Stripper	Stripper Bottoms from Cooler	Compressor Suction	Compressor Discharge	Compressor Quench Tower Spray
Mass Flow (lb/hr)	4,460	89,610	34,730	34,730	27,510
Volume Flow (scfm)	1,570	-	4,270	4,270	-

Stream Number	36	37	38	39	40
Description	Compressor Quench Overhead	Compressor Spillback from Quench	Gas Holding Drum Feed	SO_2 Rich Compressed Gas to Acid Plant	Sulfuric Acid Product To Storage
Mass Flow (lb/hr)	33,910	9,460	24,450	24,450	35,620
Volume Flow (scfm)	3,980	1,110	2,870	461	-

Stream Number	41	42	43	44	45
Description	Purge Gas to Reactors in Acceptance	NH_3 from Storage	Steam to NH_3 Vaporizer	Fly Ash from ESP	Flue Gas Recycle
Mass Flow (lb/hr)	15,500	2,475	1,520	55,000	82,000
Volume Flow (scfm)	5,720	-	530	-	17,500

Continued/

*Note: For ease of comparison with TVA's results, the values in this table are presented in English units.

TABLE 5-7. (Continued)*

Stream Number	46
Description	H_2 Vented to Boiler During Purge
Mass Flow (lb/hr)	210
Volume Flow (scfm)	430

*Note: For ease of comparison with TVA's results, the values in this table are presented in English units.

TABLE 5-8. A COMPARISON OF MATERIAL FLOWS FOR A 500 MW COAL-FIRED APPLICATION OF THE SFGT PROCESS

Stream Description	Estimated Flowrate		Ratio
	TVA	Radian	
Steam to process (kg/hr)	31,940	40,300	1.26
Hydrogen from reformer (kg/hr)	1,300	1,630	1.25
Naphtha to reformer (m^3/hr)	57	71	1.25
NH_3 to reactor (kg/hr)	830	1,120	1.35
H_2SO_4 from acid plant (kg/hr)	16,160	16,160	1.00

5.4 ENERGY REQUIREMENTS FOR A 500 MW SFGT PROCESS

The material balance presented the mass flowrates of various process streams in the SFGT process. With this as a basis, it was possible to complete an energy balance and to determine the energy requirements for a 500 MW application of the process. Determination of the energy requirements involved consideration of several factors including:

- Evaluation of the heat credits which are associated with the SFGT process,
- Determining the enthalpy of all streams entering and exiting the process; and
- Determining the electrical energy required for fans, compressors, pumps, etc., and the fuel energy required for hydrogen production.

Once each of these factors had been evaluated it was possible to determine the overall energy demands of the SFGT process.

The following discussion examines each of the above factors in detail and summarizes the estimated energy requirements of the SFGT process.

5.4.1 Evaluation of Heat Credits Associated with the SFGT Process

Due to the unique nature of the SFGT process there are several significant heat credits associated with it. The majority of these heat credits result from the location of the SFGT process which is between the economizer and the air preheater of a boiler. With the process in this location, heat generated by or added to the process can be recovered and returned to the boiler via the air preheater.

As part of the energy balance completed for the 500 MW application of the SFGT process, a quantative analysis of the process heat credits was completed. This analysis was based on the results of the material balance calculations and on pilot plant data. The specific heat credits which were considered in this analysis include:

- The heats of reaction generated by removal of SO_2, reduction of NO_x, oxidation of NH_3, oxidation of H_2 purged from the regenerated reactors, and oxidation of Cu and Cu_2S at the start of each acceptance period,
- Additional heat recovery in the air preheater due to reduction in the sulfuric acid dew point of the flue gas by removal of sulfur trioxide in the reactor,
- The work done compressing the flue gas by the flue gas blowers,
- The heat of combustion of hydrogen and other gases which slip through the reactors during regeneration, and
- The heat of combustion of hydrogen which is vented during the time reactors are being purged before and after regeneration.

The following discussion quantifies how each of these heat credits influences the overall energy consumption of the process. Since the first three heat credits result in additional heat recovery in the air preheater, individual heat credits are not quantified. Instead, an overall heat credit is determined based on the process energy balance which is discussed later in this section. The following discussion of these heat credits is limited to quantifying how they impact the overall energy balance.

Heats of Reaction

There are several chemical reactions which occur in an SFGT reactor as it processes flue gas. The acceptor is oxidized to CuO and subsequently reacts with SO_2. The acceptor also catalyzes the NO_x reduction reactions. NH_3 is oxidized in the reactor and, in addition, H_2 purged from a regenerated reactor will be oxidized.

Table 5-9 summarizes the chemical reactions which occur in an SFGT reactor during acceptance. This table also identifies the heats of reaction, and based on the material balance calculations, the quantity of heat which is added to the flue gas due to these reactions. The heat which is added to the flue gas results in an increase in the temperature of the flue gas exiting the reactor.

Based on the material balance calculations, the average temperature increase due to the heats of reaction is estimated to be approximately 50°C. However, due to the nature of the reactions which occur, instantaneous fluctuations in the temperature at the reactor outlet can be greater than 50°C. This is due to the fact that the first three reactions shown in Table 5-9 occur during the initial part of each acceptance period while the remaining four reactions occur at a relatively constant rate during the entire acceptance period. As a consequence, approximately one-third of the heat of reactions is released intermittently during each acceptance period with a resultant "spike" in the reactor outlet temperature as a function of time.

TABLE 5-9. HEATS OF REACTION WHICH ADD ENERGY TO THE FLUE GAS DURING ACCEPTANCE

Reaction	$\Delta H_{400°C}$	Heat Added to Flue Gas (Gcal/hr)
1. $Cu + \frac{1}{2}O_2 \rightarrow CuO$	-37.34 kcal/gmol Cu	6.13
2. $2Cu_2S + 5O_2 \rightarrow 2CuO + 2CuSO_4$	-103.4 kcal/gmol Cu_2S	1.79
3. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	-58.6 kcal/gmol H_2	1.34
4. $CuO + SO_2 + \frac{1}{2}O_2 \rightarrow CuSO_4$	-74.6 kcal/gmol CuO	11.97
5. $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$	-96.98 kcal/gmol NH_3	3.68
6. $2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$	-39.34 kcal/gmol NH_3	0.16
7. $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$	-75.3 kcal/gmol NH	1.58

The nature of the temperature spike which occurs early in acceptance determines what fraction of the heats of reaction can be recovered. This fraction is dependent on the thermal efficiency of the air preheater.

Air preheater thermal efficiency represents the fraction of the heat in incoming flue gas which is transferred to the combustion air. For a given air preheater design and constant mass flowrates of flue gas and air, the thermal efficiency of the preheater is independent of flue gas temperature.[7] Therefore, an air preheater designed for a given flue gas inlet temperature will only recover a fraction of the heat associated with a "spike" in flue gas outlet temperature. The fraction of heat which is recovered will be equal to the thermal efficiency of the preheater.

In order to determine what the design thermal efficiency of the preheater should be, it is necessary to define how the flue gas temperature at the reactor outlet changes as a function of time. This was done by an analysis of pilot plant data which recorded reactor outlet temperatures as a function of time. The results of this analysis for the 500 MW application of the SFGT process are presented in Figure 5-4 which illustrates the temperature at the reactor exit as a function of time for a single acceptance period. Each spike in the temperature curve represents a freshly regenerated reactor starting an acceptance period.

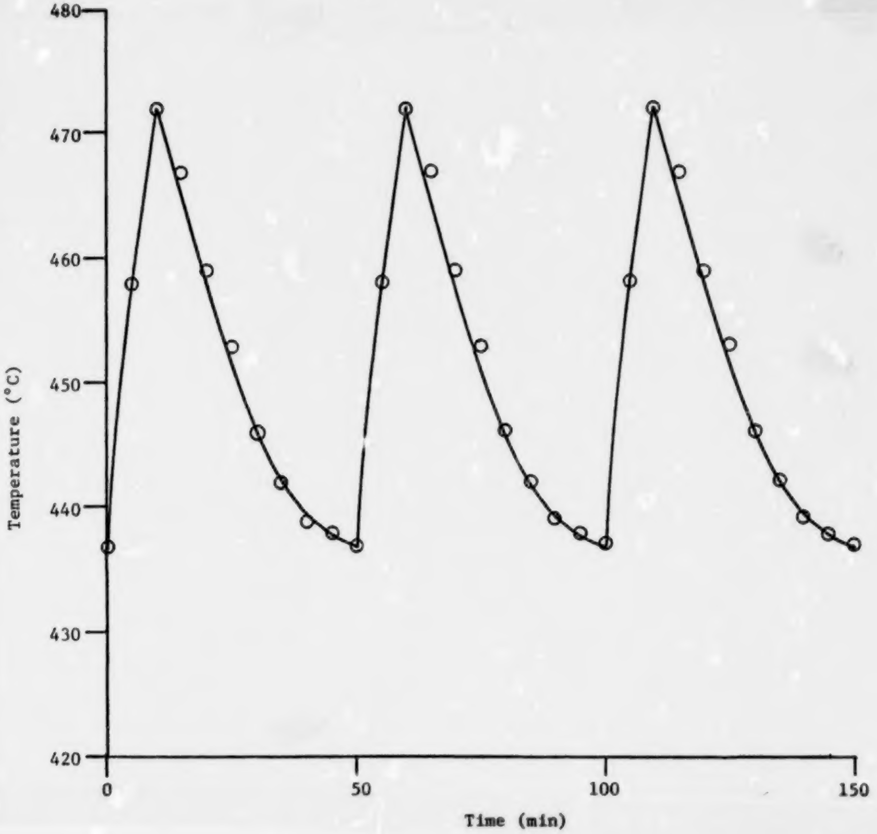

Figure 5-4. Flue gas temperature at the exit of the reactor section for a 500 MW application of the SFGT process.

As shown in Figure 5-4 the minimum temperature at the reactor exit is estimated to be 437°C while the maximum temperature is 472°C. The minimum temperature represents a temperature increase of 37°C across the reactor which accounts for all the "steady-state" heats of reaction and approximately 20 percent of the "intermittant" heats of reaction. It is the minimum temperature of 437° which serves as a basis for the air preheater design and consequently is used in determining the air preheater's thermal efficiency. This indicates that approximately 80 percent of the "intermittent" heats of reaction will be recovered at a rate equivalent to the thermal efficiency of the air preheater.

Acid Dewpoint Suppression

Another factor which influences the air preheater thermal efficiency is the temperature at which flue gas is discharged to the atmosphere. Once this temperature is determined, it is possible to calculate the air preheater thermal efficiency and therefore determine how much of the intermittent heat of reactions can be recovered. This also determines the overall heat which is recovered in the preheater and thus defines a majority of the heat credit for the SFGT process.

Based on the secondary emissions sampling conducted by Radian, it was determined that the SFGT process removes nearly all of the SO_3 from the flue gas processed in the reactor. The assumption made in completing the material balance calculations was that 90 percent of the SO_3 is removed in the reactor. This results in an SO_3 concentration of 2.6 ppm at the reactor outlet which corresponds to an acid dewpoint of approximately 124°C. Typically, this represents the absolute minimum flue gas temperature at the exit of the preheater. Temperatures below the acid dewpoint result in corrosion of equipment located downstream of the air preheater (e.g., an electrostatic precipitator). For the energy balance and heat credit analysis, the flue gas temperature at the air preheater exit was assumed to be 127°C which is about 3°C above the acid dewpoint. This temperature is equivalent to a cold-end metal temperature of about 77°C which is the low end of the air preheater manufacturer's recommended temperature, even for low-sulfur fuels.[8]

It should be noted that the presence of NH_3 in the flue gas which exits the SFGT process will eliminate the potential for formation of liquid sulfuric acid downstream of the air preheater. Instead, the SO_3 will react with NH_3 and water in the air preheater to form ammonium sulfates as illustrated by Equations 5-17 and 5-18.

$$2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4 \qquad (5\text{-}17)$$

$$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4 \qquad (5\text{-}18)$$

The temperature at which these reactions begin to occur has been estimated to be approximately 210°C which is in the intermediate temperature zone of the air preheater.[4]

In some cases, the formation of ammonium sulfate and/or ammonium bisulfate can result in corrosion and plugging problems in the air preheater. This is especially true if ammonium bisulfate is formed since this compound exists as a liquid at air preheater temperatures. Ammonium bisulfate forms deposits which adhere to air preheater surfaces, build-up, and can ultimately plug the preheater. Deposits of ammonium bisulfate can also be quite corrosive and thus reduce the service life of the heat transfer elements in the preheater.

For the 500 MW application of the SFGT process, no problems are anticipated due to formation of ammonium sulfates. It is expected that only small quantities of solid ammonium sulfate will form in the air preheater. This is due to the low concentration of SO_3 and the large excess of NH_3 in the flue gas exiting the reactor. Since ammonium sulfate exists only as a solid, any deposits which form will not adhere to the preheater surfaces nor will they be corrosive.[4]

Based on this analysis it appears that the flue gas temperature of 127°C will result in satisfactory performance of the air preheater. No corrosion of the preheater or downstream equipment would be expected. This is primarily due to the beneficial effect of the NH_3-SO_3 reactions which result in neutralization of the small amount of SO_3 which is present in the flue gas.

Work From Fan Compression

The conceptual design of the SFGT process includes a flue gas blower to overcome the pressure drop of the reactor and associated ductwork. Because the blower is located upstream of the air preheater, it is possible to recover the work done on the flue gas as heat in the preheater. The quantity of work which is added to the flue gas has been estimated to be 3.6 Gcal/hr. It should be noted that this quantity represents the theoretical work done on the flue gas and does not include inefficiencies in converting electrical energy to mechanical energy in the blower.

For purposes of evaluating the heat credits of the SFGT process and for completing an overall energy balance for a 500 MW application of the process, it was assumed that the flue gas enthalpy was increased by 3.6 Gcal/hr. This heat is therefore considered as part of the steady state heat input to the air preheater and as a consequence can be fully recovered by the preheater.

Heat of Combustion of Slipped and Vented Reducing Gas

The SFGT process does not consume 100 percent of the reducing gas generated by the steam naphtha reformer. During regeneration, a small fraction of the hydrogen and other combustable components of the reducing gas (i.e., CO and CH_4) slip through the reactor and are present in the regeneration off gas. During the period the reactor is purged before and after regeneration, the steam-naphtha reformer continues to generate reducing gas which must be vented to the boiler. Both these streams represent heat credits for the SFGT process since they can be burned and the heats of combustion recovered.

In the case of the vented reducing gas, this stream goes directly to the boiler and replaces fuel values which would normally be supplied by coal. As such, it represents a direct heat credit to the process. Based on material balance calculations, this heat credit is estimated to be 1.85 Gcal/hr.

The reducing gas which slips through the reactor is ultimately sent to the sulfuric acid plant where it is incinerated prior to processing in catalytic converters. In the incinerator, the reducing gas will burn and the heat of combustion will eventually be recovered in the form of steam. Depending on the thermal efficiency of the heat exchanger in the acid plant only a certain fraction of the heat will be recovered. For this analysis it was assumed that the thermal efficiency of the steam generator was identical to that of the boiler. This results in a direct heat credit for the slipped gas combustion which amounts to 1.91 Gcal/hr.

Heat Credit Summary

Table 5-10 summarizes the results of the heat credit analysis for the SFGT process. As shown, heat credits for heats of reaction, acid dewpoint suppression, and a compression were not analyzed separately. Instead, these credits were factored into the process energy balance and used to calculate an overall heat credit for the process. This overall heat credit is discussed in the following section.

TABLE 5-10. A SUMMARY OF SFGT PROCESS HEAT CREDITS

Heat Credit	Quantity of Heat (Gcal/hr)	Fraction Recovered (%)
Heats of Reaction		
Steady State	26.65	*
Intermittent	7.26	*
Acid Dewpoint Suppression	From 149 to 127°C	*
Fan Compression	3.60	*
Vented Gas Combustion	1.85	100
Slipped Gas Combustion	1.91	100

*The actual heat credit depends on the overall process energy balance and the air preheater thermal efficiencies. All these heat credits were factored into the energy balance which was used to estimate an air preheater thermal efficiency and to determine the overall heat credit for the process.

5.4.2 Energy Balance for the 500 MW SFGT Process

Once the SFGT heat credits were evaluated it was possible to use that information in conjunction with the results of the material balance to complete an energy balance for the SFGT process. However, one additional item which had to be defined before the energy balance could be completed was the thermal efficiency of the air preheater. This efficiency was required to determine what fraction of the intermittent heats of reactions would be recovered. The following discussion presents the calculations used to define the thermal efficiency of the air preheater. In addition, the results of the energy balance are presented and the overall heat credit for the process is quantified.

Air Preheater Thermal Efficiency

The thermal efficiency of an air preheater is defined by Equation 5-19.[7]

$$Ng = \frac{tg_{in} - tg_{out}}{tg_{in} - ta_{in}}$$

Where: tg_{in} = temperature of the flue gas entering the air preheater.

tg_{out} = temperature of the flue gas leaving the air preheater corrected for leakage.

ta_{in} = temperature of the air entering the preheater.

For the 500 MW application of the SFGT process, the uncorrected temperature of the flue gas leaving the air preheater is 127°C. Accounting for air in-leakage of 20,200 kg/hr, this corresponds to a corrected temperature of 136.4°C. The evaluation of process heat credits estimated the minimum reactor exit temperature to be 437°C. When corrected for heat removed in the steam superheater, this corresponds to an air preheater design temperature of 429.2°C. For an air inlet temperature of 26.7°C, the estimated air preheater thermal efficiency is 72.8 percent.

The thermal efficiency represents the fraction of heat entering the air preheater in the flue gas which is recovered in the combustion air. It also represents the fraction of the intermittent heats of reaction which are recovered by the preheater.

Results of Energy Balance Calculations for the 500 MW Application of the SFGT Process

An energy balance was prepared for a 500 MW application of the SFGT process. This energy balance considered all the major streams entering and exiting the process. In addition, the heat credits discussed in the preceding section along with the heats of the regeneration reactions were included. It should be noted that the energy balance does not represent a comprehensive evaluation of the energy requirements of the process since it does not include electrical and fuel energy requirements. These are considered later in this section.

The results of the energy balance calculations for the 500 MW application of the SFGT process are summarized in Table 5-11. The energy associated with major inputs and outputs are shown for flue gas streams and steam flows. These energy balance results include all the heat credits discussed in the preceding section along with credits for the exothermic regeneration reactions. In addition, the results presented in Table 5-11 include steam which is generated in the sulfuric acid plant and the steam naphtha reformer.

There are several assumptions implicit in Table 5-11 which influence the overall heat credit and energy balance for the SFGT process. First, the NH_3-air mixture is assumed to enter the process at 38°C. Since most of this gas stream is eventually discharged from the air preheater at a corrected temperature of 136.4°C, an energy penalty of approximately 1 Gcal/hr results. This energy penalty could potentially be eliminated if, instead of air, flue gas was used as a carrier for the NH_3.

TABLE 5-11. SUMMARY OF ENERGY BALANCE CALCULATIONS FOR 500 MW APPLICATION OF SFGT PROCESS

Stream Description	Enthalpy (Gcal/hr)
Gas Streams to Process	
• Flue Gas to Blower	199.09
• NH_3-Air Mixture	0.35
• Hydrogen for Regeneration	1.36
• Combustion Air to Air Heater	13.75
Gas Streams from Process	
• Flue Gas to ESP	74.03
• Combustion Air to Boiler	169.60
Steam to Process	
• Steam to Superheater	25.04
• Steam to NH_3 Vaporizer	0.45
• Steam to Stripper	1.32
Steam from Process*	
• Steam from Waste Heat Boiler	6.02
• Steam from Acid Plant	8.98
• Steam from Reformer	4.32
• Condensate from Flow Smoothing	1.35

*These stream enthalpies are net changes due to the process.

A second assumption which influences the energy balance is that the hydrogen stream enters the process at 400°C. If this stream was cooler it would result in an energy penalty. For example, if the hydrogen enters the process at 38°C as opposed to 400°C the energy penalty would be about 1.2 Gcal/hr.

Finally, the results presented in Table 5-11 show a significant energy credit for steam generated in the reformer and the sulfuric acid plant. This credit results in nearly a 70 percent decrease in the overall steam requirements for the SFGT process. The quantity of steam generated in the acid plant and reformer was estimated based on TVA's preliminary economic analysis.

Overall Heat Credit for the SFGT Process

The information presented in Table 5-11 can be used to estimate the overall heat credit for the SFGT process. This can be done by comparing the enthalpy of flue gas and combustion air streams for the same 500 MW power plant with and without application of the SFGT process. The results of such a comparison are presented in Table 5-12. As shown, the overall heat credit for the SFGT process is estimated to be 31.98 Gcal/hr not including heat credits for combustion of vented and slipped reducing gas.

TABLE 5-12. ESTIMATED OVERALL HEAT CREDIT

Stream Description	Enthalpy (Gcal/hr) W/SFGT	W/O SFGT	Δ
1. Flue Gas from Economizer	199.09	191.39	7.7
2. Combustion Air to Preheater	13.75	13.75	0
3. Combustion Air to Boiler	169.60	129.92	39.68
4. Heat Recovered in Air Preheater (3 - 2)	155.85	116.17	39.68
5. Overall Heat Credit* (Δ 4 - Δ 1)	-	-	31.98

*This does not include heat credits for vented and slipped gas combustion.

The overall heat credit shown in Table 5-12 represents the difference between additional heat which is recovered in the combustion air preheater downstream of the SFGT process and that recovered without SFGT minus the additional heat which enters the SFGT process in the flue gas. This heat credit represents the net effects of the heats of reactions, acid dewpoint suppression, and fan compression on the overall energy balance. With the addition of heat credits for vented and slipped gas combustion, the overall heat credit for the 500 MW application of the SFGT process is estimated to be 35.75 Gcal/hr.

5.4.3 Electrical and Fuel Energy Requirements

The two components of the overall energy requirements of the SFGT process which have not yet been defined are the electrical energy requirements and fuel energy requirements. Electrical energy is required to operate fans, compressers, and pumps and for operation of the steam naphtha reformer and the sulfuric acid plant. Fuel energy is consumed by the process as naphtha in the reformer. In conjunction with process steam requirements and the overall heat credits, these energy requirements can be used to define the overall energy requirement for the 500 MW application of the SFGT process.

The following discussion presents the results of calculations which were used to estimate the electrical and fuel energy requirements of the SFGT process. These calculations used both the material balance calculations presented in Section 5.2 and TVA's preliminary economic analysis as a basis.

Electrical Energy Requirements

Electrical energy requirements were estimated for the pumps, fans, and compressers used in the SFGT process. This estimate was prepared by determining the theoretical work required by each item of equipment and assuming an efficiency of 70 percent for conversion of electrical energy to mechanical work. In the case of the steam-naphtha reformer and the sulfuric acid plant, the electrical energy requirements were determined by a direct ratio of the electrical energy requirements from TVA's preliminary cost estimate.

The estimated electrical energy requirements for a 500 MW application of the SFGT process are summarized in Table 5-13. As shown, the single largest energy requirement is that associated with the main flue gas blower. This accounts for over 40 percent of the total electrical energy. The other major energy requirements include the electrical energy required for operation of the sulfuric acid plant and the energy required to operate the SO_2-rich gas compressor.

TABLE 5-13. ESTIMATED ELECTRICAL ENERGY REQUIREMENTS FOR a 500 MW APPLICATION OF THE SFGT PROCESS

Process Equipment Item	Theoretical Energy Requirement (kW)	Estimated Actual Energy Requirement (kW)
NH_3 Compressor	126	180
SO_2-Rich Gas Compressor	656	937
Quench Water Circulating Pump	228	326
Stripper Bottoms Pump	6	8
NH_3 Injection Blower	10	15
Flue Gas Blower	4206	6008
Steam Naphtha Reformer	-	313
Sulfuric Acid Plant	-	2050
	Total Electrical Energy Requirements	9837

Fuel Energy Requirements of the Process

The fuel energy required by the SFGT process is that energy which could be obtained by burning the naphtha used to generate hydrogen in the reformer. Based on the hydrogen requirements defined in the material balance and the naphtha requirements defined by TVA, the naphtha requirements for the 500 MW application of the SFGT process are estimated to be 7.1 m^3/hr. The heat of combustion of the naphtha is 8.89 Gcal/m^3 so the total fuel energy requirement for the 500 MW application of the SFGT process is approximately 63 Gcal/hr.

5.4.4 Overall Energy Requirements for the 500 MW Application of the SFGT Process

The preceding discussion has defined the basis for and presented the results of calculations which estimate the individual components of the energy requirements for a 500 MW application of the SFGT process. This section summarizes these results and puts the individual components of the process energy requirements on a common basis.

Table 5-14 presents the individual components and the estimated overall energy requirements for a 500 MW application of the SFGT process. Each of these components has been put on the basis of heat input to the boiler. For steam, a thermal efficiency of 88 percent was used to determine the energy input required to generate one Gcal of steam energy. For electricity, a boiler heat rate of 2.27 Mcal/kWh was used. The heat credits and fuel energy requirements were assumed to replace heat input to the boiler on a 1-to-1 basis.

TABLE 5-14. OVERALL ENERGY REQUIREMENT FOR A 500 MW APPLICATION OF THE SFGT PROCESS

Energy Area	Energy Requirement (Gcal/hr)	Percent of Boiler Capacity
Heat Credit	(35.75)	(3.2)
Steam	6.98	0.6
Electricity	22.3	2.0
Fuel	63.0	5.6
TOTAL	56.53	5.0

As shown in Table 5-14, the overall energy requirement for the 500 MW application of the SFGT process is 55.7 Gcal/hr which represents 5 percent of the boiler's capacity. The single largest component of this energy requirement is the fuel energy associated with the naphtha used to generate hydrogen. And as shown, the heat credit represents a significant reduction in overall energy requirements for the process.

5.5 ESTIMATED COSTS FOR A 500 MW APPLICATION OF THE SFGT PROCESS

The final step in the evaluation of the SFGT process was to prepare a modified cost estimate for a 500 MW application of the process. This cost estimate includes an estimate of both capital costs and annual revenue requirements. It was prepared to show how the results of the pilot plant tests affected the economics of the process. Because the estimate used the same basis as TVA's preliminary economic analysis, the results can be used to compare SFGT process costs with the costs of other SCR processes. It should be noted, however, that the comparison is only for a specific application of the SFGT process and the results may not be valid for other applications. This is due to the fact that the costs of the SFGT process can vary as a function of SO_2 concentration in the flue gas while the costs of applying other SCR processes will not.

The procedure used in preparing the estimate of capital costs and annual revenue requirements was to first define equipment costs for the process. This was done using TVA's original equipment cost list and standard exponential capacity factors for chemical process equipment. Installation costs for piping, insulation, foundations, etc. were estimated as a percentage of the equipment costs. Once the installed equipment costs were defined, the total capital costs and annual revenue requirements were estimated. The estimates of these costs used factors developed by TVA along with the results of the conceptual design and material and energy balances developed as part of this study.

The following discussion presents the results of the estimates of capital costs and annual revenue requirements for the SFGT process. It includes a brief discussion of how the estimates were derived and a comparison of the modified SFGT cost estimate with the costs of other SCR processes as determined by TVA. A detailed discussion of the economic premises used to prepare the cost estimates along with an estimate of individual equipment item costs is presented in Appendix D of this report.

5.5.1 Estimated Total Capital Investment for a 500 MW Application of the SFGT Process

Procedure for Estimating Capital Investment

The capital cost estimate for the SFGT process was based primarily on the costs of process equipment. These costs were estimated for individual items of process equipment using the equipment costs developed by TVA as a basis. Modified equipment costs were determined by comparing process flowrates for individual equipment items and using cost-size exponents which reflect equipment cost-size relationships typical of the chemical process industry. In the case of the copper-aluminia acceptor material, it was assumed that no economy of scale was realized (i.e., the cost per unit cell of acceptor material is constant). Using this procedure, the costs for individual equipment items were determined. These costs should accurately reflect modified costs since, in nearly all cases, the size did not vary significantly from the equipment sizes in the original cost estimate. These costs are representative of a Midwestern power plant location and mid-1979 dollars. The costs were not escalated to 1981 dollars in order to facilitate comparison with estimated costs for other SCR processes.

Once equipment costs were determined, the various installation expenses such as piping, foundations, etc., were estimated as a percentage of equipment costs. The sum of the process equipment costs and installation expenses constituted the major components of the direct investment. The final component of the total direct investment includes a services and miscellaneous cost which was calculated as percentages of the installed equipment cost. The sum of the installed equipment cost and the services and miscellaneous cost is the total direct investment.

The total indirect investment (the sum of various indirect investments, such as engineering design and supervision, A&E contractor, construction expense, and contractor fees) was calculated based on the total direct investment using formulas described in Appendix D of this report. A contingency, calculated as 20% of the sum of the total direct and total indirect investment, was also included. The sum of the total direct investment, the total indirect investment, and the contingency equals the total fixed investment.

Other capital charges included in the cost estimates consist of an allowance for startup and modification, interest during construction, land costs, working capital. The allowance for startup and modification and interest during construction were calculated as a percentage of the total fixed investment, the previously calculated allowance for startup and modification, and interest during construction. The sum of total depreciable investment, land costs, and working capital is the total capital investment.

Results of Capital Cost Estimate

Table 5-15 presents the individual components and the estimated total capital investment for a 500 MW application of the SFGT process. As shown, the total capital investment was estimated to be approximately $\$84.2 \times 10^6$ which is equivalent to \$168/kW of generating capacity. This compares to TVA's previous estimate of $\$67.2 \times 10^6$ and it represents about a 25 percent increase in total capital investment. The principal difference between the two estimates is the estimated acceptor volume. The required acceptor volume was estimated to be nearly 90 percent greater based on the pilot plant tests with the resultant increase in total capital investment.

TABLE 5-15. ESTIMATE CAPITAL INVESTMENT FOR A 500 MW APPLICATION OF THE SFGT PROCESS[a]

	Investment, $	% of total direct investment
Direct Investment[b]		
NH_3 storage and injection	890,000	1.9
H_2SO_4 plant	7,172,000	15.2
Reactor section	27,455,000	58.1
Flow smoothing section	2,828,000	6.0
Steam Naphtha reformer	4,698,000	9.9
Gas handling	1,546,000	3.3
Sub-total direct investment (DI)	44,589,000	94.4
Services, utilities (0.06 x DI)	2,675,000	5.6
Total direct investment	47,264,000	100.0
Indirect Investment		
Engineering design and supervision	709,000	1.5
Architect and engineering contractor	177,000	0.4
Construction expense = 0.25 $(TDI \times 10^{-6})^{0.83}$	6,135,000	13.0
Contractor fees = 0.096 $(TDI \times 10^{-6})^{0.76}$	1,799,000	3.8
Total indirect investment (IDI)	8,820,000	18.7
Contingency = 0.2 (TDI + IDI)	11,217,000	23.7
Total fixed investment (TFI)	67,301,000	142.4
Other Capital Charges		
Allowance for startup and modifications = (0.1) (TFI)	6,730,000	14.2
Interest during construction = (0.12) (TFI)	8,076,000	17.1
Total depreciable investment	82,107,000	173.7
Land	14,000	-
Working Capital	2,051,000	4.4
TOTAL CAPITAL INVESTMENT	84,172,000	178.1

[a] Basis: 500 MW new coal-fired power plant, 3.5% sulfur coal, 90% NO_x removal, 90% SO_2 removal. Midwest plant location. Represents project beginning mid-1977, ending mid-1980. Average basis for scaling, mid-1979. Investment requirements for fly ash disposal excluded. Construction labor shortages with overtime pay incentive not considered.

[b] Each item of direct investment induces total equipment costs (presented in Appendix D) plus installation labor, and material costs for electrical, piping, ductwork, foundations, structural, instrumentation, insulation and site preparation.

The principal reason for the increased acceptor requirements was due to the high NO_x slip at the start of each acceptance period. This initially poor NO_x removal resulted in the requirement for extended acceptance periods to permit the time averaged NO_x reduction to reach the 90 percent level. The longer acceptance period required additional acceptor to maintain the time averaged SO_2 removal efficiency at the 90 percent level. As a consequence the capital costs of the process increased significantly.

It should be noted that it may be possible to reduce the estimated capital investment by reducing the NO_x slip at the start of each acceptance. One technique for reducing initial NO_x slip which was examined during the pilot plant tests was the use of preoxidation and cooling step following regeneration. The use of a preoxidation and cooling step was quite successful in the pilot plant tests and its introduction into a commercial design may be one way of reducing total capital investment. It should also be noted that because of the long acceptance time required to achieve 90 percent NO_x reduction, the SO_2 concentration can have a significant impact on total capital investment for the process. At lower SO_2 concentrations (i.e. less than 2590 ppm) the quantity of acceptor required to maintain SO_2 removal efficiency at 90 percent will also be lower. Therefore, the capital investment would be expected to decrease at lower design SO_2 concentrations.

5.5.2 Estimated Average Annual Revenue Requirements for a 500 MW Application of the SFGT Process

Procedure for Estimating Annual Revenue Requirements

The annual revenue requirements were calculated based on a Midwestern power plant location and mid-1980 costs. These average annual revenue requirements were divided into the direct costs, which consists of raw materials costs and conversion costs and indirect costs, which consist of capital charges and overheads.

In calculating direct costs, the raw material, utility, and labor unit costs used were those developed by TVA while the required quantities of these cost items were based on the conceptual design and the material and energy balance results. The maintenance cost was calculated as a percentage of total direct investment.

The capital charges portion of the indirect costs consists of: (1) depreciation, interim replacements, and insurance, which were estimated based on the total depreciable investment; and (2) the average costs of capital and taxes, which were determined based on the total capital investment. The overhead charges consist of: (1) plant overhead, which was estimated as a percentage of the cost of operating labor and supervision, maintenance, and analyses; and (2) administrative overheads, which were estimated based on a percentage of operating labor and supervision. Specific details of how each of the components of the annual revenue requirements was estimated are presented in Appendix D.

The annual revenue requirements were determined as the sum of the direct and the indirect costs. Equivalent unit revenue requirements in mills/kWh were then obtained by dividing by the on-stream time of 7000 hr/yr and the plant MW rating.

Results of the Annual Revenue Requirement Estimate

Table 5-16 presents the individual components and the total estimated average annual revenue requirements for a 500 MW application of the SFGT process. As shown, the average annual revenue requirement was estimated to be approximately $\$33.6 \times 10^6$/yr which is equivalent to 9.60 mills/kWh. This compares to TVA's previous estimate of $\$22.5 \times 10^6$/yr and represents nearly a 50 percent increase in the annual revenue requirements for the process.

As with the capital costs, the principal factor which increased the annual revenue requirements is the increased quantity of acceptor required in the reactor. Additional acceptor as a raw material accounts for over

TABLE 5-16. ESTIMATED AVERAGE ANNUAL REVENUE REQUIREMENTS FOR A 500 MW APPLICATION OF THE SFGT PROCESS[a]

Item	Annual Quantity	Unit Cost($)	Annual Cost($)	% of Annual Revenue Required
Direct Costs				
Raw Materials				
NH_3	7.87x10^{6}kg	0.165/kg	1,299,500	3.87
Naphtha	39,773 m^3	132.1/m^3	5,254,000	15.65
Catalyst	-	-	12,600,300	37.53
Reformer Catalyst	-	-	125,100	0.37
Total Raw Materials			19,278,900	57.42
Conversion Costs				
Operating Labor and Supervision	29,200 labor hrs	12.50/ labor hr	365,000	1.09
Utilities				
naphtha	9,943 m^3	132.1/m^3	1,313,500	3.91
steam	42,970 Gcal	7.94/Gcal	341,200	1.02
process water	8,078,000 m^3	0.23/m^3	128,000	0.38
electricity	68,859,000 kWh	0.029 kWh	1,996,900	5.95
heat credit	250,200 Gcal	-7.94/Gcal	(1,896,000)	(5.65)
Maintenance			1,891,000	5.63
Analyses	4,380 labor hrs	17.00/labor hr	74,500	0.22
Total Conversion Costs			4,214,100	12.55
Total Direct Costs			23,493,000	69.97
Indirect Costs				
Capital Charges				
Depreciation = (0.06) x (total depreciable investment)			4,926,400	14.67
Average cost of capital = (0.086) x (total capital investment)			7,238,800	21.56
Overheads				
Plant = (0.5) x (conversion costs minus utilities)			1,165,300	3.47
Administrative = (0.1) x (operating labor costs)			36,500	0.11
Marketing = (0.1) x (sales revenue)			366,000	1.09
Total Indirect Costs			13,733,000	40.90
Spent Catalyst Disposal			11,400	0.03
Gross Average Annual Revenue Requirement			37,237,400	110.90
Byproduct Sales Revenue				
H_2SO_4	11.1 x 10^{6}kg	-0.033/kg	(3,660,000)	(10.90)
TOTAL ANNUAL REVENUE REQUIREMENTS			33,577,400	100.00

[a] Basis: 500 MW new coal-fired power plant 3.5% S coal. 90 percent NO_x reduction, 90 percent SO_2 removal. Midwest power plant location, 1980 revenue requirements. Remaining life of power plant = 30 years. Plant on line 7000 hr/yr. Plant heat rate equals 2.27 Mcal/kWh. Investment and revenue requirement for disposal of fly ash excluded. Total direct investment $47,264,000; total depreciable investment $82,107,000; and total capital investment $84,172,000.

50 percent of the increase in annual revenue requirements in addition to the effect of additional acceptor costs on the capital charges. Another significant factor which increased annual revenue requirements is the estimated increase in naphtha required for hydrogen generation. This accounts for about 12 percent of the increase in annual revenue requirements. Other increases result from a decreased estimate of the heat credit, increased NH_3 usage, and an increase in the capital charges for the process.

5.5.3 A Comparison of Capital Investment and Annual Revenue Requirements of the SFGT Process with a Conventional NOx Only SCR Process

The capital investment and annual revenue requirements of the SFGT process have been estimated based on the results of the tests conducted at the EPA sponsored pilot unit in Tampa, Florida. The results of these cost estimates indicate that the capital costs and annual revenue requirements are higher than the estimated costs prior to the test program. A more significant indication of how the pilot plant results affect SFGT process costs is a comparison of SFGT process costs to the costs of a NO_x only SCR process.

Since the same basis was used in preparing the modified SFGT cost estimate as TVA used in preparing preliminary economic estimates for other SCR processes, it is possible to make a direct comparison with TVA's previously published results and the results of EPA's evaluation of the Hitachi Zosen process. Table 5-17 shows the estimated capital investment for the two pollution control systems which reduce emissions of particulates, NO_x and SO_x by 99.5, 90, and 90 percent respectively. As shown, the pollution control systems employ two SCR processes, one being the SFGT process. The HZ SCR process is coupled with a flue gas desulfurization system and both processes have ESP's located downstream in order to put the cost estimates on a common basis.

TABLE 5-17. ESTIMATED CAPITAL INVESTMENT FOR TWO POLLUTION CONTROL SYSTEMS[1]

SCR Process	Total Capital Investment ($ x 10^{-6})			
	SCR	FGD	ESP	Overall
SFGT	84.2	-	14.6	98.8
Hitachi Zosen	22.1	50.4	10.8	83.3

[1] All costs except the SFGT-SCR and HZ SCR costs are from "Preliminary Economic Analysis of NO_x Flue Gas Treatment Processes". Tennessee Valley Authority - Office of Power, EPA - 600/7-80-021, February, 1980. HZ SCR costs are from "Independent Evaluation of the Hitachi Zosen NO_x Flue Gas Treatment Process". Radian Corporation - Draft Report. January, 1982.

As shown on Table 5-17, the SFGT process requires a larger capital capital investment having a capital cost approximately 17 percent higher than the HZ process. This indicates that the SFGT process probably does not represent the most economic SCR system for this particular 500 MW application. However, within the accuracy of the cost estimates defined by TVA (-20 to +40 percent) the SFGT process may still be competitive. In addition, the dependence of SFGT capital costs on flue gas SO_2 concentration may make its relative capital costs more favorable at lower SO_2 concentrations.

Table 5-18 presents the annual revenue requirements for the two pollution control systems. As shown, the estimated costs associated with the SFGT processes are approximately 35 percent higher than those of the pollution control system which employs a NO_x only SCR process. The principal reasons for the higher costs include increased quantity of acceptor required by the SFGT process, and the higher capital charges for the process.

The results presented in Table 5-18 indicate that the SFGT process, as tested in the pilot plant and presented in the conceptual design, is probably not competitive with a NO_x only SCR process for the 500 MW application examined in this study. Again, the relative costs presented in Table 5-18 are only valid for one specific application and they could change for applications with lower SO_2 concentrations in the flue gas.

TABLE 5-18. ESTIMATED ANNUAL REVENUE REQUIREMENTS FOR TWO POLLUTION CONTROL SYSTEMS[1]

SCR Process	Total Capital Investment ($ x 10^{-6}			
	SCR	FGD	ESP	Overall
SFGT	33.6	-	3.0	36.6
Hitachi Zosen	10.2	14.7	2.2	27.1

[1] All costs except the SFGT-SCR and HZ SCR costs are from "Preliminary Economic Analysis of NO_x Flue Gas Treatment Processes". Tennessee Valley Authority - Office of Power, EPA - 600/7-80-021, February, 1980. HZ SCR costs are from "Independent Evaluation of the Hitachi Zosen NO_x Flue Gas Treatment Process". Radian Corporation - Draft Report. January, 1982.

5.6 OVERALL EVALUATION OF THE SFGT PROCESS

The preceding discussion has examined many factors which influence the technical and economic feasibility of applying the SFGT process to a coal-fired boiler. These factors include:

- the pilot plant test results,
- the results of Radian's Independent Tests,
- the results of the 500 MW conceptual design,
- the material balance calculations for the 500 MW SFGT process application,
- the energy balance calculations for the 500 MW SFGT process application, and
- the estimated capital investment and annual revenue requirements for the 500 MW SFGT process application.

In order to put all these factors into perspective and thereby complete the evaluation of the SFGT process, a summary of the most significant results was prepared. This summary, which is presented in the following discussion, identifies how the results of the tests and calculations influence the feasibility of applying the SFGT process to a coal-fired power plant. In addition, the summary identifies areas not addressed during the pilot plant tests.

5.6.1 Pilot Plant Test Results

The objective of the pilot plant tests conducted by UOP was to demonstrate simultaneous reduction of NO_x and SO_2 emissions by 90 percent during 90 days of continuous operation. While this objective was not met, the tests did document the technical feasibility of applying the SFGT process to a coal-fired power plant. The pilot plant operated for approximately 2000 hours without soot blowing and with no signs of plugging in the reactor. Although the total time the pilot unit processed flue gas is less than what would be expected during 1 year of commercial operation, the tests do indicate that plugging of the reactor should not present a problem for a commercial application.

In terms of process performance, the pilot plant tests did not demonstrate simultaneous reduction in NO_x and SO_2 emissions under design operating conditions. Ninety (90) percent NO_x/SO_2 reduction was achieved through the use of a preoxidation and cooling step, which UOP now proposes to include in future process designs. The pilot unit test results can be extrapolated to determine the ability of the process to reduce NO_x and SO_2 emissions by 90 percent without preoxidation and cooling. This requires the use of additional acceptor which can significantly impact the estimated costs for the SFGT process.

The test program briefly examined the effects of key operating parameters but did not provide a detailed characterization of the effects of those parameters on process performance. Two parameters in particular, temperature and flowrate, were shown to affect process performance, yet their effects were not thoroughly documented. Temperature and flowrate are significant parameters since they would be expected to change as boiler load changes, thus changing NO_x and SO_2 emission reduction efficiencies. Because the separate and combined effects of these parameters were not the subject of detailed characterization, the conceptual design prepared as part of this study incorporated two features which are not common to all SCR processes. These factors are: (1) temperature control to maintain constant flue gas temperature at the reactor inlet, and (2) open recycle of processed flue gas to maintain a constant flowrate though the reactor. Without further documentation of the effects of reduced load on SFGT process performance, it is expected that any commercial coal-fired application of the process would require control of both temperature and flowrate at the reactor inlet.

Probably the most important aspect of the SFGT process performance which was documented during the pilot plant tests was the stability of acceptor activity. The test results showed that upon first exposure to flue gas, acceptor activity experienced an initial decline but then remained stable over the course of 700 hours of operation. This is a favorable sign in terms of applying the process to a coal-fired boiler since, after the initial decline, there was no measurable change in activity. Although not a goal of the test program, this did not document acceptor activity over a period of time equivalent to 1 year of commercial operation. It is critical to the economic feasibility of the SFGT process that stable acceptor activity be maintained over at least 1 year of operation. And, if the acceptor can maintain activity for longer than a year, a significant reduction in process costs would be realized. This could make the process more cost competitive with other SCR processes. It should be noted that (1) the cost estimate prepared during this study is based on a 1 year acceptor life and (2) UOP will guarantee a 1 year acceptor life.

Overall, the pilot plant test results indicate that application of the SFGT process to a coal-fired boiler is technically feasible. However, these tests did not demonstrate several key factors, including:

- the ability of the process to simultaneously reduce NO_x and SO_2 emissions by 90 percent at design operating conditions,
- the performance of the process under conditions which simulate reduced boiler loads, and

- the stability of the acceptor over a period equivalent to 1 year of commercial operation.

Of these factors, the one most critical to the commercial success of the process is the stability of the acceptor. This is probably the single-most significant factor in determining process costs. If the acceptor life is less than 1 year, the costs for the process are expected to preclude its use. While a longer acceptor life makes the process more competetive economically.

5.6.2 Results of the Independent Evaluation Test Program

The independent evaluation test program conducted by Radian had two primary objectives: to insure the quality of the data collected at the SFGT pilot plant, and to quantify changes in the concentrations of certain pollutants across the SFGT reactor. As discussed earlier, the results of the quality assurance audits and certification tests validated the process data collected by UOP. These results have no direct bearing on the overall feasibility of the SFGT process with one exception. As a result of the inability to monitor NH_3 in the flue gas, the NH_3 emission measurements, made as part of the QA audits, represent a significant portion of the data based on NH_3 emissions from the process. These data, in conjunction with the results of the secondary emissions sampling tests quantify the secondary environmental impact associated with the SFGT process as it was operated during the pilot unit tests.

The results of the secondary emissions sampling program indicated that no measurable change occurred in the concentrations of trace elements in the particulates passing through the reactor or in the concentrations of HCN or nitrosoamines in the flue gas. In the case of particulates, the results show that no environmental problem will occur due to erosion (if any) of the acceptor. In the case of HCN and nitrosoamines, the concentrations of these compounds were below the detection limit of the analytical techniques employed and were also below the maximum safe concentrations for emission sources. Again, this indicates that no environmental problem will occur due to production of these compounds.

Other results of the secondary emissions sampling program indicated that the concentrations of CO, HC's and SO_3 all decreased across the reactor. In the case of CO and HC's, this indicates a slight environmental benefit would result from application of the process. However, the ability of the process to reduce CO and HC's emissions does not have a significant influence on overall process feasibility. The removal of SO_3, on the other hand, does impact the economic feasibility of the process. Removal of SO_3 results in a reduction in the acid dewpoint which permits additional heat recovery in the air preheater. The economic benefits of reduced acid dewpoint are multiplied since this also permits more efficient recovery of the heats of reaction and the heat of fan compression which are added to the flue gas by the SFGT process.

The NH_3 emissions measured during the pilot plant tests indicated that during cyclic operation, no significant operational or environmental problem would be expected to result from these emissions. However, as discussed during the conceptual design development, these emissions are not expected to be representative of an SFGT process designed for 90 percent reduction of NO_x and SO_2. Changes in reactor design, inlet NO_x concentration and NH_3/NO_x injection ratio can result in a significant increase in the NH_3 emissions. Any increase in NH_3 emissions is not expected to present an operational problem due to the low concentration of SO_3 in the flue gas. In addition, thermodynamic calculations indicate that NH_3 in excess of that which reacts with SO_3 will react with HCl to form NH_4Cl. The NH_4Cl will form solid particles which should be collected in an ESP. Previous studies have indicated that environmental problems can result from high NH_3 concentrations in fly ash depending on the specifics of fly ash disposal techniques.[9] However, for most applications, no environmental problems would be expected.

One compound scheduled to be measured during the secondary emissions sampling program was N_2O. However, the analytical technique used to make the N_2O measurements proved unsatisfactory. Therefore, no determination was made on whether any significant quantity of N_2O was being produced in the reactor. Any future development work on the SFGT process should include provisions for measurement of N_2O.

Overall, the independent evaluation tests indicated that:

- no emissions problems resulted from application of the SFGT process with the exception of NH_3,
- the levels of NH_3 emissions measured during the pilot plant tests should not present either environmental or operational problems,
- the NH_3 emissions measured during the test program may not be representative of a full scale application but even increased levels of NH_3 emissions should not present an operational problem due to the low concentrations of SO_3 in the flue gas which exits the SFGT reactor,
- environmental problems can occur depending on the specific details of the fly ash disposal techniques. However, for most applications, no problems are expected, and
- it was not possible to determine the concentration of N_2O (if any) in the reactor outlet. This requires further investigation.

Generally these results show that there are no significant emissions problems associated with the SFGT process. N_2O production represents one possible exception, but there are currently no regulations which limit the emission rate of this compound.

5.6.3 Results of the 500 MW Conceptual Design

The conceptual design of the SFGT process was prepared for a single application of the SFGT process and it was based solely on the pilot plant test results. The results of this design indicate that it is technically possible to simultaneously reduce NO_x and SO_2 emissions by 90 percent using the SFGT process. However, the quantity of acceptor required to meet the design NO_x and SO_2 reduction efficiencies is significantly greater than previous estimates indicated.

To some extent, the increase in the quantity of acceptor is a function of the limitations placed on the conceptual design to reflect pilot plant operation. Data were collected which indicated substantial improvement in NO_x and SO_2 reduction efficiencies could be achieved but limitations of the pilot plant prevented adequate characterization of process performance under modified operating conditions.

Another cause for the increased acceptor requirements was the poor NO_x reduction efficiencies of the pilot unit at the start of each acceptor period. This resulted in the requirement for long acceptance times to permit the time averaged NO_x reduction efficiency to reach 90 percent. For the SO_2 concentration used in preparing the conceptual design, longer acceptance times resulted in a corresponding increase in acceptor requirements. It appears that at lower flue gas SO_2 concentrations, the impact of increased acceptance times would not have as significant an effect on the acceptor requirements.

Reactor pressure drop and other design parameters are fairly consistent with previous estimates for the process. The results do, however, indicate the need for equipment to control the temperature and flowrate of the flue gas entering the reactor. This is primarily due to the fact that data were not developed to characterize overall process performance under conditions which simulated reduced boiler loads.

In summary, the conceptual design indicates that the SFGT process can simultaneously reduce NO_x and SO_2 emissions by 90 percent. However, this level of emissions reduction is achieved only at the expense of an increased quantity of acceptor and a corresponding increase in costs. It should be noted that there may be other means of improving process performance, but these were not considered in preparing the conceptual design. (In fact, UOP now proposes to include preoxidation and cooling steps in future process designs.) Further development work should be aimed at identifying operating/design conditions which result in 90 percent NO_x/SO_2 reduction at lower acceptor volumes.

5.6.4 Results of the Material Balance Calculations

Material balance calculations for a 500 MW application of the SFGT process were included as part of this study to identify raw material requirements for the process and to serve as a basis for the cost estimate which was presented in Section 5.5. The material balance was based on the pilot plant and secondary emissions sampling test results and thus reflects those results in the estimated raw material requirements. The most significant results of the material balance calculations include estimation of hydrogen and steam requirements for regeneration, NH_3 requirements for NO_x reduction, and NH_3 and SO_3 emissions from the process.

The hydrogen requirements for the 500 MW applications were estimated to be approximately 3 moles of H_2 per mole of SO_2 removed from the flue gas. This compares to a mole ratio of 4.2 in the pilot plant and a ratio of 2.4 in TVA's preliminary economic analysis for the SFGT process. As discussed in Section 5.3, the H_2 requirements were estimated based on pilot plant data and the assumption that unaccounted for H_2 is consumed due to formation of Cu_2S. If no Cu_2S formation occurs, the estimated H_2/SO_2 mole ratio for the conceptual design would be 2.6 which represents a 13 percent reduction in H_2 consumption. This reduction in H_2 requirements is accompanied by a corresponding decrease in naphtha requirements, energy consumption, and process costs. Obviously, the assumption of Cu_2S formation can have a significant impact on process costs.

During the pilot plant tests, several attempts were made by UOP to quantify Cu_2S formation in the reactor. Although these attempts proved unsuccessful they did indicate some Cu_2S was forming in the reactor. Because the attempts to quantify Cu_2S formation were unsuccessful, the best measurement of Cu_2S formation is the H_2 material balance used to estimate H_2 requirements for the 500 MW application. Further work is required to better estimate the quantity of Cu_2S which forms in the reactor and to examine the factors which influence it (e.g., steam to H_2 ratio). This would document expected H_2 requirements and possibly indicate ways to reduce the H_2 consumption by the process.

The steam required for regeneration was estimated directly from the H_2 requirements and the pilot plant tests results. During the pilot plant tests the steam/H_2 ratio was approximately 4. This same ratio was used in preparing the 500 MW material balance. It should be noted that steam requirements would also be reduced if no Cu_2S formation occurs in the reactor.

The NH_3 requirements for this process were determined from the conceptual design which was based on the pilot plant test results. The NH_3/NO_x injection ratio of 1.5 was significantly greater than previous estimates and it resulted in over a 35 percent increase in NH_3 requirements for the process. While this increase in NH_3 consumption does not significantly impact process costs, it does result in relatively high estimated NH_3 emissions (49 ppm). However, these emissions are not expected to present operating problems due to the low estimated concentration of SO_3 in the flue gas exiting the reactor (<3 ppm).

In summary, the material balance calculations showed significant increases in the requirements for H_2 (25 percent), superheated steam (29 percent), and NH_3 (25 percent) over TVA's preliminary estimate. Of these, increased H_2 consumption has the most significant impact on process costs and process energy requirements (due to increased naphtha requirements). Also, the factors which influence H_2 consumption are not well defined and in particular the factors which influence Cu_2S formation were not investigated. Further investigation of the process should examine the factors which influence H_2 consumption in more detail.

5.6.5 Results of the Energy Balance Calculations

An energy balance was completed as part of the evaluation of the SFGT process. This energy balance defined overall process energy requirements and quantified the heat credits associated with the process. The results of the analysis of energy requirements indicated that the SFGT process has a net energy consumption equivalent to 5 percent of the energy input to the boiler.

The single largest component of the overall energy requirement is the fuel energy which could be obtained by burning the naphtha used to generate hydrogen. This represents over 5 percent of the equivalent energy consumed by the boiler and it is directly dependent on the H_2 requirements of the process. Because the fuel energy requirement is so large, a given percentage decrease in H_2 requirements would result in approximately an equivalent percentage decrease in overall energy requirements for the process. This is a strong basis for further examination of H_2 requirements and the factors which affect H_2 consumption.

The energy requirements associated with steam and electrical energy are less than 50 percent of the fuel energy requirements. In the case of steam, this represents a small fraction of the overall energy requirements of the process and although some reduction in steam consumption may be possible, it will not significantly influence the annual revenue requirements. In the case of electrical energy, the major portion of this requirement results from the energy of fan compression. This can be reduced by reducing acceptor volume. As discussed earlier, additional development work may demonstrate the viability of operating at reduced acceptor volume.

The heat credits associated with the SFGT process were estimated to be equivalent to over 3 percent of the energy input to the boiler. And these credits result in nearly a 40 percent decline in the overall energy requirements for the process. The heat credit analysis indicates that nearly all of the potential heat credits are recovered. A small fraction of the intermittent heats of reaction are lost due to limitations of the air preheater but this is not significant in terms of the overall heat credit. Also, a small reduction in the overall heat credit results from using air as a carrier for NH_3. It would be possible to eliminate this heat loss if flue gas was used instead of air.

Overall, the largest component of the SFGT process energy requirement is the naphtha used to generate hydrogen. This is significant from several standpoints. First, the costs of naphtha represent a large fraction (∿20 percent) of the annual revenue requirements for the process. Second, due to the current energy supply situation, the costs of naphtha could escalate rapidly and thus have an even more significant impact on the annual revenue requirements of the process. For these reasons, future development work should focus on reducing H_2 requirements for the process and/or demonstrating the use of alternative reductants (e.g., CO, CH_4, etc.)

5.6.6 Results of the Cost Estimate for the 500 MW SFGT Process Application

An estimate of total capital investment and annual revenue requirements for a 500 MW application of the SFGT process was prepared as part of this evaluation. The estimated costs reflect the results of the pilot plant tests. When compared with the previous estimate prepared by TVA, the modified cost estimates indicate the magnitude of the impact the pilot plant results had on estimated process costs. In addition, comparison of the modified cost estimate with cost estimates for other SCR processes is a relative indicator of the cost effectiveness of the SFGT process as tested in the pilot plant.

The capital costs for the SFGT process were estimated to be $\$84.2 \times 10^6$ which represents a 25 percent increase over TVA's preliminary estimate. This was primarily due to the increased quantity of acceptor required by the conceptual design and it indicates that the performance of the pilot plant was significantly poorer than previous estimates expected. This was in part due to lower than expected SO_2 removal efficiency of the acceptor which may have resulted from the unique application of the pilot plant. However, the principal cause of the increased acceptor requirements and consequent increased costs was the poor NO_x reduction efficiencies measured at the start of each acceptance period. The initially poor NO_x reduction resulted in the requirement for longer acceptance times to achieve a time averaged NO_x reduction efficiency of 90 percent. Longer acceptance times translate into increased acceptor requirements which significantly impact costs.

As discussed earlier, it is possible to reduce acceptor requirements through the use of preoxidation and cooling. But this technique was not demonstrated in a manner consistent with commercial operation. In addition, there may be other techniques for reducing initial NO_x slip (e.g., leaving a fraction of the acceptor sulfated), but these techniques were not examined in detail during the pilot plant tests. Therefore, further development work should focus on identifying and demonstrating methods for reducing the initial NO_x slip during the acceptance period. This could significantly reduce capital investment requirements for the SFGT process.

The estimated annual revenue requirements for the SFGT process were $\$33.6 \times 10^6$ which represent nearly a 50 percent increase over TVA's preliminary estimate. This increase is primarily due to the increased quantity of acceptor required based on the pilot plant test results. As discussed earlier, it may be possible to reduce the acceptor requirements in several ways. Another factor in determining annual revenue requirements is acceptor life. Table 5-19 presents estimated annual revenue requirements as a function of acceptor life. As shown, a 6-month acceptor life results in about a 40 percent increase in costs compared to the base case (1 year life) while a 2-year life results in nearly a 20 percent decrease in costs. Obviously, if a 2-year acceptor life could be demonstrated a significant reduction in annual revenue requirements would result.

TABLE 5-19. ESTIMATED ANNUAL REVENUE REQUIREMENTS AS A FUNCTION OF ACCEPTOR LIFE

Acceptor Life	Annual Revenue Requirements $\$ \times 10^{-6}$
Base Case (1 year)	33.6
6 months	46.2
2 years	27.3

Overall the results of the modified cost estimate indicate that, for the particular SFGT application examined in this study, the SFGT process does not appear to be economically competitive with other SCR processes. This is based on a conceptual design which was limited to operating conditions demonstrated during the pilot plant tests. It is possible that estimated costs would change significantly for a design based on operating conditions which were not examined in detail during the pilot plant tests (e.g., the use of a preoxidation and cooling step in the process). It is also possible that SFGT process costs may be more competitive with the costs of other SCR processes for lower sulfur coal applications.

For the estimates presented in this evaluation, a 1-year life was assumed. This was not demonstrated during the pilot plant tests and so costs could vary significantly from those estimated in this study. Further development work should focus on defining acceptor life and on demonstrating alternate operating/design conditions designed to minimize acceptor requirements.

5.6.7 Process Evaluation Summary

The preceding discussion has identified the factors which influence the technical and economic feasibility of the SFGT process along with some of the limitations of this evaluation. This section summarizes the most significant aspects of the evaluation and presents an overall conclusion concerning the technical and economic feasibility of applying the SFGT process to a coal-fired power plant.

The most significant results of the pilot plant test program and this evaluation are:

- The SFGT process can simultaneously reduce NO_x and SO_2 emissions by 90 percent when applied to a coal-fired boiler. However, this level of emissions reduction can only be attained at the expense of increased acceptor volume (over the pilot plant design) or through the use of operating and/or design options which were tested only for a short period during the pilot plant test program.

- No problems with reactor plugging or declining acceptor activity were evident during the pilot plant test program. This indicates that the copper oxide acceptor and the parallel passage reactor design appear technically suited for application to a coal-fired source. The pilot plant tests did not, however, demonstrate a stable acceptor life equivalent to 1-year of commercial operation. While this was not an objective of the test program, it must be verified to establish the technical and economic feasibility of the process.

- The secondary emissions sampling program indicated no adverse environmental impacts would result from applications of the SFGT process as operated during the pilot plant tests. However, the measured NH_3 emissions may not be representative of a full-scale application of the process. Also, it was not possible to measure N_2O emissions (if any) from the process so the question of N_2O production remains unanswered.

- The secondary emissions sampling program did establish the fact that the SFGT process removes SO_3 from the flue gas. This represents a significant benefit for the process since removal of SO_3 permits recovery of additional heat in the air preheater. In addition, the low concentrations of SO_3 measured at the reactor outlet should preclude any problems with plugging and corrosion of the preheater due to the formation of ammonium sulfates.

- The conceptual design and material balance calculations indicated that significant increases (over TVA's preliminary estimate) in H_2, steam, and NH_3 consumption are expected based on the pilot plant test results. Of these, H_2 consumption has the greatest impact on the economic feasibility of the process. Since a detailed characterization of the factors which influence H_2 consumption was not completed during the pilot plant tests, it may be possible to reduce H_2 consumption. This represents an area which warrants further investigation.

- The overall energy balance indicated that the SFGT process has an energy requirement equivalent to 5 percent of the energy input to the boiler for a 500 MW application. When combined with an ESP, the SFGT process requires about 50 percent more energy than other SCR systems combined with ESP's and FGD systems. The principal component of the overall process energy requirement is the fuel energy associated with the naphtha used to generate hydrogen.

- Nearly all of the potential heat credits available to the SFGT process can be recovered which results in reducing overall process energy requirements by about 40 percent. The most significant fraction of the heat credits which cannot be recovered is equivalent to about 20 percent of the intermittent heats of reaction (e.g., the heat of reaction for Cu oxidation). The fraction of intermittent heats of reaction recovered is limited by the thermal efficiency of the air preheater which, for this evaluation, was estimated to be about 73 percent.

- The estimated total capital investment and average annual revenue requirements for the SFGT process are significantly higher than the costs for other SCR processes combined with FGD systems. This indicates that the SFGT process is not economically competitive with other SCR systems for the case examined as part of this evaluation. However, there are alternative applications of the SFGT process which may be more economically competitive. The alternatives include use of operating and/or design options not examined during the pilot plant tests and thus not demonstrated for coal-fired applications. In addition, applications of the process on sources firing low-sulfur coal could be more economically competitive.

In conclusion, the pilot plant test results indicate the SFGT process is technically suited for application to coal-fired sources. However the tests did not demonstrate a 1-year acceptor life which is generally considered a minimum for technical feasibility of an SCR process. (It should be noted that this was not an objective of the test program.) In reality, a shorter acceptor life would translate into increased annual revenue requirements, and make the process uneconomical when compared to other SCR processes.

In terms of costs, the SFGT process does not appear economically competitive with NO_x only SCR processes for high sulfur coal applications. It may be more competitive for low sulfur coal applications, but this evaluation did not quantify costs for such an alternative. In addition, there are several techniques which could reduce overall process costs, but these were not demonstrated during the pilot plant test program.

SECTION 6

PROCESS DEVELOPMENT REQUIREMENTS

The pilot plant test results and the evaluation completed as part of this study have defined many of the factors which affect the technical and economic feasibility of applying the SFGT process to a coal-fired source. However, due to limitations of the pilot plant test program, there are several key factors which were not examined. These factors represent process development requirements of varying priorities; some must be examined in further test work to establish the technical or economic feasibility of the process and some simply represent methods of improving process performance or lowering process costs. This section presents a discussion of the process development requirements identified during the course of the independent evaluation program. It also defines priorities for further investigation of those requirements.

The process development requirements identified during the course of this study include:

- Determination of acceptor life for coal-fired applications.
- Demonstration of commercially applicable technique(s) for reducing NO_x slip at the start of acceptance.
- Examination of the factors which affect H_2 consumption by the process.
- Demonstration of the use of reductants such as CH_4 or CO for regeneration of the reactor.
- Demonstration of the ability of the process to maintain design performance levels under conditions which simulate reduced load.
- Determination of NH_3 emissions from the process over a range of conditions which simulate commercial operation.

- Quantification of N_2O emissions (if any) from the process.

- Demonstration of an automatic NH_3 injection control system including a continuous NH_3 analyzer.

Each of these development requirements represents an area not addressed during the pilot plant tests and therefore an unanswered question concerning the SFGT process. The following discussion examines each requirement in more detail and discusses its importance in terms of the technical and economic feasibility of the SFGT process.

Acceptor Life

The useful life of the copper oxide acceptor for a coal-fired application of the SFGT process was not determined during the pilot plant tests. The test results did show that acceptor activity experienced an initial decline when flue gas was first processed in the reactor. Following this initial decline, there was no measurable change in acceptor activity over a 700 hour period. While these results indicate activity was stable they cannot be extrapolated to determine the acceptor life.

The question of acceptor life for a coal-fired application is the single most important one remaining concerning the SFGT process. As discussed earlier, acceptor life has a very significant impact on annual revenue requirements for the process. And, it will ultimately determine whether the SFGT process is economically competitive with other SCR processes. If the acceptor life is longer than the life of other SCR catalysts it will make the SFGT process more competitive.

Because the results of the SFGT process evaluation indicated that, for the application examined, the process was not competitive with other SCR processes, the primary goal of future development work should be aimed at establishing the acceptor life for coal-fired applications. This can be done in either pilot plant or larger scale tests but it is a question which must be answered.

Initial NO_x Slip

During the pilot plant tests, the NO_x slip at the start of each acceptance period was quite high. This contributed to the inability of the pilot plant to meet the original objectives of the test program (i.e. simultaneous reduction of NO_x and SO_2 emissions by 90 percent for 90 days). In addition, using the NO_x slip curves generated during the demonstration test as a basis for the conceptual design resulted in a required acceptor volume significantly greater than previous estimates indicated. This, in turn, resulted in a significant increase in the estimated costs for the SFGT process.

Because of the dependence of process performance and costs on initial NO_x slip, operating and/or design options which reduce the initial slip can improve the economic competitiveness of the SFGT process. During the pilot plant test program, UOP examined several techniques for reducing the initial NO_x slip including:

- NH_3 injection delay,
- partial regeneration of the acceptor, and
- preoxidation and cooling of the acceptor.

NH_3 injection delay and partial regeneration did not significantly improve the overall process performance. As a result, detailed process data were not collected to document the effects of employing these techniques. Preoxidation and cooling was the most successful of the techniques and therefore was examined in the most detail. However, the preoxidation and cooling technique was not implemented in a manner consistent with commercial operation of the SFGT process. Consequently, none of these techniques were considered in developing the conceptual design and none of them can be considered demonstrated.

The pilot plant test results did indicate the potential for reduced NO_x slip at the start of acceptance using the techniques discussed above. In addition, there may be other techniques or design options which can be employed to reduce initial NO_x slip. Since a reduction in initial NO_x slip can be accompanied by lower process costs, further work should be conducted to examine techniques for reducing initial NO_x slip. In terms of priority, this is not considered as critical as demonstrating the acceptor life but it can have a very significant impact on overall process costs.

Hydrogen Consumption

Hydrogen was employed as a reductant during the pilot plant tests to regenerate the sulfated acceptor. The reactions which consume H_2 during regeneration include the reduction of both $CuSO_4$ and CuO to elemental copper. In addition, evidence indicates that some H_2 may be consumed as a result of Cu_2S formation during regeneration.

During the pilot plant tests, several attempts were made to quantify Cu_2S formation in the reactor. And although these tests did indicate evidence of Cu_2S formation, it was not possible to determine the exact fraction of acceptor which was present as Cu_2S. As discussed earlier, the fraction of acceptor which forms Cu_2S can have a significant impact on estimated H_2 requirements for the process and consequently on overall process energy requirements. The energy balance results indicate that if H_2 requirements are reduced by a given fraction, overall energy requirements will be reduced by about the same fraction with a consequent drop in annual revenue requirements.

Since Cu_2S formation can impact energy requirements and process costs, a better estimate of Cu_2S formation could improve the accuracy of estimated process costs. Further, examination of the factors which control Cu_2S formation could lead to methods of reducing H_2 consumption and thus the annual revenue requirements of the process. For these reasons, further development work on the SFGT process should include tests to quantify and possibly minimize Cu_2S formation. It should be noted that the potential reduction in process costs due to minimization of Cu_2S formation is not as significant as the potential cost reductions associated with determining acceptor life or decreasing initial NO_x slip. Consequently, this area of investigation is of lower priority.

Other Reductants

Hydrogen was used as a reductant during the pilot plant test program for several reasons with the principal one being the H_2 is the most reactive reductant with respect to the regeneration reactions. In terms of commercial operation, use of H_2 as a reductant does not currently present any significant problems. H_2 can be generated easily and relatively inexpensively through the use of steam naphtha reforming. However, due to uncertainties in the future supply and perhaps more importantly, future costs of liquid fuels, the exclusive use of H_2 could present a problem. For this reason it would be desirable to demonstrate the use of other reductants or a mixture of reductants as suitable regeneration feed gas.

Initially the pilot plant program called for tests in which a reducing gas similar in composition to low-Btu gas produced from coal would be used as regeneration feed gas. However, other tests took priority, and the tests using simulated low-Btu gas were never run. Since the reasons for conducting those tests still exist (i.e., the projected availabilities of solid and liquid fuels) further development work should include examination of reductants other than H_2. The priority of this development work is considered low since no immediate problem exists. However, projected increases in liquid fuel prices could significantly impact estimated annual revenue requirements for the process in the future.

Low Load Simulation

The effects of varying temperature and flowrate on process performance were examined during the pilot plant tests. However, process performance was never quantified under conditions which simulated low boiler loads. For this reason, the conceptual design prepared as part of this evaluation included two features designed to maintain constant conditions of temperature and flowrate to the reactor. These features are: control of the heat removed from the flue gas by the economizer and an open recycle loop which results in constant flow to the reactor. These features were considered a necessary part of the conceptual design since it was not possible to predict process performance under conditions of reduced boiler load.

In preparing the cost estimate, no additional capital costs were included for the temperature control system since these costs were not expected to be significant. In addition, the costs associated with open recycle which were included were not a significant fraction of overall costs. As a consequence the inclusion of temperature control and open recycle will slightly increase SFGT process costs but there is no strong economic incentive for further investigation of the effects of temperature and flowrate on process performance. However, documentation of process performance at simulated low-load conditions could improve the flexibility of the processes and thus broaden its applicability. The priority of this work is considered low in terms of demonstrating the applicability of the SFGT process to a coal-fired source.

NH_3 Emissions

NH_3 emissions from the SFGT process are not expected to present any operating problems for equipment located downstream of the SFGT process. This is primarily due to the low SO_3 concentrations at the reactor outlet which preclude the formation of significant quantities of ammonium sulfates (and in particular liquid ammonium bisulfate). In addition, for most applications no environmental problems are expected. Over 90 percent of the NH_3 which exits the reactor should be collected in an ESP as ammonium chloride particulates. However, in some cases, high NH_3 emissions (greater than 30 ppm) can result in violation of the EPA Water Quality Criteria for NH_3. The level of NH_3 emission which can cause problems is dependent on many factors and in particular, the quantity of NH_3 in the fly ash and the characteristics of the fly ash handling and disposal system of the boiler.[9]

For most power plant applications, no environmental problem would be expected for projected levels of NH_3 emissions. However, since the potential does exist for problems to occur, it would be useful to accurately characterize NH_3 emissions from the SFGT process under conditions which simulate a full scale application. As discussed earlier, the NH_3 emissions measured during the pilot plant test may not be representative of a commercial design. For this reason, further development work on the process should include tests designed to characterize NH_3 emissions over a range of operating conditions and reactor designs typical of commercial operation. Quantification of NH_3 emissions in this manner should permit identification of any potential problems for a specific application. Since NH_3 emissions are not expected to present a significant problem in most commercial applications, the priority of further development work in this area is considered low.

N_2O Emissions

Originally, the secondary emissions sampling program included tests to measure N_2O production in the SFGT reactor. Unfortunately, the techniques used during the sampling program did not prove satisfactory and it was not possible to measure N_2O in the flue gas streams. As a result, the question of N_2O production in the reactor remains unanswered.

Currently there are no regulations which limit N_2O emissions from stationary sources. One reason for this is because significant quantities of N_2O are not produced as a result of stationary source combustion. However, production of large quantities of N_2O could present problems not typically encountered. For this reason, further development work should include tests designed to characterize N_2O emissions (if any) from the SFGT process. Based on the poor performance of the infrared analyzer used for the secondary emissions sampling program, the recommended technique is cryogenic trapping followed by gas chromatography analysis. This involves concentration of N_2O in the gas stream followed by quantitative analysis and is routinely used to measure concentrations of N_2O as low as 0.3 ppm.

Since there are no regulations which limit N_2O emissions, the priority of development work designed to quantify these emissions is considered low.

NH_3 Injection Control/Continuous NH_3 Analysis

Automatic control of the NH_3/NO_x injection ratio and the use of continuous NH_3 emission measurements as feedback to such a control system represents an area not addressed during the pilot plant tests. The NH_3 injection control system employed during the test program was completely manual; the NH_3 flowrate to the reactor was set by an operator at a value calculated to produce a desired NH_3/NO_x injection ratio. As a result, changes in flue gas NO_x concentration (due to changes in boiler load) resulted in significant fluctuations in the NH_3/NO_x injection ratio.

Obviously it would be desirable to demonstrate an automatic NH_3 injection control system. This minimizes NH_3 consumption and limits the amount of operator attention needed to operate the SCR system. In addition, the use of continuous NH_3 emissions measurements as feedback would tend to minimize NH_3 emissions from the process.

In most operating SCR systems in Japan, the NH_3 injection rate is controlled by a feed forward system based on the desired NH_3/NO_x injection ratio, the flue gas flowrate, and the NO_x concentration of the flue gas. Because of the number of installations operating this type of control system, it can be considered as commercially available. The type of control system which has not been demonstrated is that which uses NH_3 emission measurements as feedback. The reason for this is the lack of a continuous NH_3 analyzer. This represents a research and development requirement not only for the SFGT process but for SCR processes in general.

During the pilot plant tests, UOP attempted to measure NH_3 emissions continuously using a converter-analyzer system which oxidizes NH_3 to NO_x and then measures the NO_x using a chemiluminescent analyzer. This technique did not prove successful, although the exact problem(s) with the technique was never determined. Currently, there is quite a bit of research being done in

Japan and the U.S. to develop a continuous NH_3 analyzer, but to date no technique has been demonstrated. Further work in this area should focus on evaluating the various techniques being developed and demonstrating the most promising ones. In the case of the SFGT process this does not represent a significant development requirement since NH_3 emissions are not expected to present significant problems. But for other SCR systems, feedback control of the NH_3 injection rate could be used to minimize potential operating problems with downstream equipment (in particular the air preheater).

Summary

In summary, there are development requirements for the SFGT process of varying priorities. Of these, the most significant is demonstration of a 1 year or greater acceptor life for coal-fired applications. Other significant requirements include, (1) development and demonstration of techniques to reduce initial NO_x slip with a consequent reduction in acceptor volume required to reduce NO_x and SO_2 emissions by 90 percent, and (2) examination of Cu_2S formation in the reactor to determine if the estimated H_2 consumption can be reduced. The other development requirements discussed in this section are of lower priority and they do not represent significant obstacles for commercial application of the SFGT process.

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APPENDIX A

QUALITY ASSURANCE AUDIT RESULTS

TECHNICAL NOTE

RESULTS OF THE QUALITY ASSURANCE AUDITS AT THE EPA SPONSORED NO_x PILOT PLANTS

April, 1981

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SECTION 1

INTRODUCTION

The Environmental Protection Agency sponsored pilot scale tests of two selective catalytic reduction (SCR) processes for NO_x removal. The processes tested were the Hitachi-Zosen (HZ) process and the Shell flue gas treatment (SFGT) process which also removes SO_2. The contractors responsible for design and operation of these pilot units were Chemico Air Pollution Control Corporation (HZ process) and the Process Division of UOP (SFGT process). In both cases, these contractors were responsible for collection, evaluation, and reporting of test data.

As part of the pilot scale test program, EPA contracted Radian Corporation to conduct an independent evaluation of the performance of both pilot units. This independent evaluation consisted of several steps including:

- A quality assurance program to check measurements being made by the process operators,
- A sampling program to quantify changes in secondary process emissions across the SCR reactors, and
- A program to certify the performance of the continuous NO_x monitors (and SO_2 monitors at the SFGT pilot unit) using EPA reference methods.

This technical note presents the results of the quality assurance (QA) audits conducted to insure the quality of the major process measurements made by Chemico and UOP. Results of the secondary emissions sampling program and the continuous monitor certification tests are contained in separate technical notes.

SECTION 2

OBJECTIVES AND APPROACH

The objective of the Quality Assurance audits conducted by Radian was to provide an independent check of the major process measurements made on a routine basis by both UOP and Chemico. Not all process measurements were subject to audit as part of the QA program. Only those measurements which are most significant in terms of quantifying process raw material and energy requirements were audited.

Table 1 summarizes the QA audit plan. It identifies the process measurements to be audited, the planned audit frequencies, and the techniques used to conduct the QA audits at both pilot plants. As shown, these process measurements represent the most basic operating parameters required to characterize the operation of the HZ and SFGT processes. The principal raw material requirements are characterized by the quantity of NH_3 required to reduce a specific quantity of NO_x and, in the case of the SFGT process, the quantity of H_2 needed to regenerate the acceptor. The major utility requirements are characterized by the power needed to overcome the reactor pressure drop and the steam required. The flue gas flowrate is required to complete material balances and to determine the capacity of the reactor and thus the costs to treat a specific volume of gas. Ammonia emissions are important since they can have potentially significant operational and economic impacts on equipment located downstream of an SCR system. And finally, flue gas SO_2 concentration was audited at the HZ pilot plant to document the ability of the catalyst to operate treating flue gas with relatively high SO_2 concentrations.

The techniques used to conduct the QA audits represent independent checks on the process measurements. In several cases the techniques used were EPA reference methods while others represent standard instruments or sampling and analytical methods. In the case of NH_3 emissions measurements, care was taken to insure that the formation of ammonium sulfates did not interfere with the sampling and analysis procedure.

The audit frequencies presented in Table 3-8 were selected based on several criteria. One consideration in specifying the audit frequencies was the availability/reliability of continuous process measurements. The most significant item which was not measured continuously at either pilot plant was the NH_3 concentration at the reactor outlet. As a consequence, the planned audit frequency for this measurement was relatively high.

Another consideration in determining the audit frequencies was the difficulty of making a particular measurement. If an audit is very time consuming then obviously this reduces the number of audits which can be conducted in a given period of time. An example of this is the H_2 flowrate at the SFGT pilot unit. It was expected that auditing the H_2 flowrate measurement would be difficult and so the frequency was lower.

It should be noted that the audit frequencies specified in Table 1 were initial frequencies and they changed as the QA program progressed. For the most part a change in audit frequency depended on the agreement between the audit result and the value of the process measurement recorded by Chemico or UOP.

Figure 1 presents a decision chain which was used as one basis for changing the initial audit frequencies, depending on the agreement between process measurements and the audit results. As shown, if the agreement was within ±5 percent, the audit frequency was decreased and the new frequency determined by the on site QA program leader. If the audit agreement was within ±10 percent of the measured value, no change in frequency was made.

TABLE 1. SUMMARY OF THE QA AUDIT PROGRAM

Process Measurement/ Location	Pilot Plant Audited[1]		Initial Audit Frequency (Audits/Week)	Audit Procedure
	HZ	SFGT		
SO_2 Concentration/ Reactor Inlet	X		2	EPA Method 6
Flue Gas Flowrate	X	X	3	EPA Method 2
NH_3 Injection Rate	X	X	3	Absorption followed by weight gain measurement - analogous to EPA Method 4
Reactor Pressure Drop	X	X	3	Magnehelic differential pressure gauge
Reactor Operating Temperature	X	X	3	Thermocouple with traverse of gas duct
NH_3 Concentration/ Reactor Outlet	X	X	10	Absorption, distillation and titration
Steam Flowrate		X	0.5	Calibration of orifice plate
H_2 Flowrate		X	0.5	

[1] X indicates an audit was scheduled.

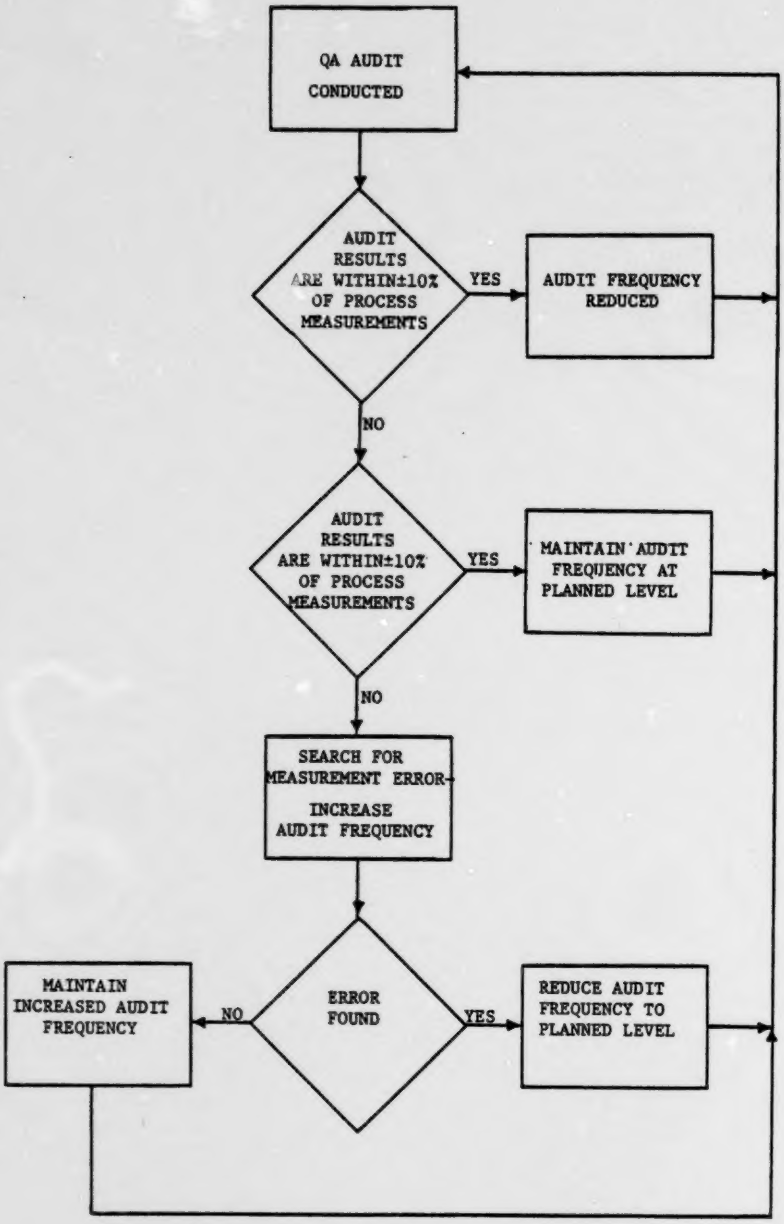
QA AUDIT CONDUCTED
AUDIT RESULTS ARE WITHIN±10% OF PROCESS MEASUREMENTS
YES
AUDIT FREQUENCY REDUCED
NO
AUDIT RESULTS ARE WITHIN±10% OF PROCESS MEASUREMENTS
YES
MAINTAIN AUDIT FREQUENCY AT PLANNED LEVEL
NO
SEARCH FOR MEASUREMENT ERROR-
INCREASE AUDIT FREQUENCY
ERROR FOUND
NO
MAINTAIN INCREASED AUDIT FREQUENCY
YES
REDUCE AUDIT FREQUENCY TO PLANNED LEVEL

Figure 1. Action plan based on QA audit results.

If the audit agreement was outside the ±10 percent range, corrective action was initiated to determine the source of error in either the audit procedure or the process measurement. At the same time, the audit frequency was increased. If the source of error was found and corrected, the audit frequency was reduced. However, if the error could not be resolved, the audit frequency was maintained at the maximum practical level within the time and manpower limits of the program. In addition to the use of relative accuracy of the QA audits as a basis for modifying the audit frequency, several practical considerations resulted in the reduction of the audit frequencies. These are discussed in Section 3.

SECTION 3

RESULTS OF THE QA AUDITS

The planned QA audits and the audit procedures were outlined in Section 2 of this technical note. This section presents a summary of the QA audits and details of individual audit results. It also includes a brief discussion of the results.

Summary

Table 2 summarizes the QA audit results from both the HZ and the SFGT pilot plants. As shown, most of the QA audit results were within 10 percent of the process measurements made by UOP and Chemico. This indicates that these process measurements were accurate and the test data collected can be used to characterize process operation.

Two measurements which did not show good agreement with the QA audits were the SO_2 concentration at the HZ pilot plant and the flue gas flowrate at the SFGT pilot plant. In both cases, subsequent investigation resolved the discrepancy between the process measurements and the QA audits.

In the case of the flue gas SO_2 concentration at the HZ pilot plant, the audit results were determined to be correct and the SO_2 monitor was in error. This error is characteristic of the type of SO_2 monitor used (pulsed fluorescence) when the instrument is calibrated with standard gases composed of SO_2 in nitrogen. The response of a pulsed fluorescence SO_2 monitor to SO_2 in a gas stream is quenched by the presence of O_2 and CO_2. This means that addition of O_2 and CO_2 to a gas stream contining SO_2 and N_2 will result in an apparent reduction in the concentration of SO_2 as measured by a pulsed

TABLE 2. RESULTS OF THE QA AUDITS AT BOTH THE HZ AND SFGT PILOT PLANTS

Process Measurement/ Location	Planned Audit Frequency (Audits/Week)	Relative Error(%)	Actual Frequency (Audits/Week)	Relative Error(%)	Actual Frequency (Audits/Week)
SO_2 Concentration/ Reactor Inlet	2	-19.8	2	NA[1]	NA
Flue Gas Flowrate	3	-0.3	2	-14.4	2.5
NH_3 Injection Rate	3	-6.0	1	7.6	1
Reactor Pressure Drop	3	4.5	2	-1.4	2
Reactor Operating Temperature	3	4.8	2	-1.3	2
Steam Flowrate	0.5	NA	NA	ND[2]	0
H_2 Flowrate	0.5	NA	NA	ND	0

[1] NA - Not Applicable

[2] ND - Not Determined

fluorescence analyzer. The error which results from calibration with SO_2-N_2 mixtures (this was done at the HZ pilot plant) can be as high as 30 percent.

In the case of the flue gas flowrate measured at the SFGT pilot plant, the audit was determined to be in error. Because of the discrepancy between the process measurement and the audit result, UOP made an independent check of the flue gas flowrate measurement. The results of this independent check agreed very well with the process measurement results. It was concluded that the duct area used to calculate flowrate for the EPA Method 2 tests (velocity traverse) was in error. This may have been due to a measurement error or blocking of a portion of the duct crossection by fly ash.

Table 2 does not present the results of NH_3 emission tests conducted at the pilot plants. These results are contained in Appendix B with the secondary emissions sampling results. The reason for this is that continuous NH_3 monitor at both pilot plants did not work and so, the NH_3 emission "audit results" represented a large fraction of the NH_3 emission measurements at both pilot plants and were not actually audits. (Both Chemico and UOP did conduct batch sampling and analysis tests for NH_3).

Table 2 also indicates that two measurements scheduled to be audited were not. Both the steam and H_2 flowrates were not audited because it was not possible to do so without shutting down the SFGT pilot plant operation. However, following the completion of the demonstration tests, the orifice plates used to measure steam and H_2 flowrates were calibrated by UOP personnel.

Finally the planned and actual audit frequencies are presented in Table 2. As shown, most of the actual audit frequencies are lower than the planned frequencies. There are several reasons for this discrepancy. In the case of reactor pressure drop, the flue gas inlet temperature, and the flue gas flowrate at the HZ plant, the agreement was excellent (±5 percent), and the frequency was reduced according to the decision chain shown in Figure 1. In the case of NH_3 injection rate, the agreement was good (±10 percent) and the difference was constant so no benefit was derived from a large number of audits. At the SFGT pilot plant, the audit frequency for the flue gas flowrate was ultimately limited by access to the flue gas stream. The sampling locations at the reactor inlet and outlet had to be shared between personnel conducting the QA audits and those conducting the stack sampling and continuous monitor certification tests.

Only the audit frequency for flue gas SO_2 concentration was as originally scheduled. However, the QA plan called for an increase in audit frequency if the relative error was greater than 10 percent. The audit frequency was not increased in this case since the difference between the SO_2 monitor results and the QA audits was relatively constant.

Overall, the QA audit results indicated that the process measurements made at both pilot plants were accurate. One exception was the SO_2 measurements at the HZ pilot plant. The audit results and subsequent investigation revealed the SO_2 monitor was in error by about 20 percent. This, however, does not affect the overall process evaluation since SO_2 was measured to document the concentration of SO_2 the catalyst was exposed to and not as a key process parameter.

The following discussion presents the results of individual QA audits.

SO_2 Concentration

Table 3 presents the results of the QA audits of the flue gas SO_2 monitor at the HZ pilot plant. As shown, the relative error was quite high averaging nearly 20 percent.

TABLE 3. HZ SO_2 MONITOR QA AUDIT RESULTS

Test No.	Continuous Monitor (ppm)	Method 6 (ppm)	Error (%)
1	990	1248	-20.7
2	1000	1271	-21.3
3	960	1256	-23.6
4	990	1207	-18.0
5	1000	1156	-13.5
6	960	1216	-21.1
Average	983	1226	-19.8

This was due to the quenching effect of O_2 and CO_2 on the pulsed fluorescence monitor used to measure flue gas SO_2 concentrations at the HZ pilot plant. Investigators conducted an analysis of pulsed fluorescence analyzers and determined the error could be as high as 30 percent. The following equation was developed to correct the monitor's results based on the flue gas composition.

$$(K_{SO_2} \cdot P_{SO_2} + K_f)\,(I_o/I-1) = P_{O_2} \cdot K_{O_2} + P_{CO_2} \cdot K_{CO_2} + (P_{N_2} - 760\ I_o/I)K_{N_2}$$

Where I_o = Intensity without quenching

I = Intensity with quenching

K_i = Quenching rate for species i (i.e., SO_2, O_2, CO_2, N_2)

P_i = Partial pressure of species i

K_f = Fluorescence decay rate

Using the average flue gas composition and solving this equation for I_o, the corrected SO_2 concentration can be estimated. However, experimental values for K_i's need to be determined. These data are not available at this time.

As a rough estimate, the results of the QA audits of the SO_2 monitor indicate that the SO_2 concentrations measured by Chemico were 20 percent lower than the actual flue gas concentration. Fortunately, these data do not affect the overall process evaluation.

Flue Gas Flowrate

The results of the flue gas flowrate QA audits at the HZ and SFGT pilot plants are presented in Tables 4 and 5 respectively. As shown, the flowrate audits at the HZ pilot plant were in excellent agreement with the measurements made by Chemico, indicating that the process measurements were accurate. However, the flowrate measurements at the SFGT pilot plant did not agree with the audit results. As discussed earlier, it appears that the audit result was inaccurate. The consistent error between the process measurements and the audit results indicates that the actual audit measurement (flue gas velocity rather than flowrate) was accurate and a consistent error was introduced in the flowrate calculation. The most likely explanation for this is that an inaccurate value for the duct crossection was used in the flowrate calculations.

The QA flowrate audit results indicate that accurate flowrate measurements were made at both the HZ and SFGT pilot plants.

TABLE 4. HZ FLUE GAS FLOWRATE QA AUDIT RESULTS

Test No.	Flowmeter (scfm)	Audit - Method 2 (scfm)	Error (%)
1	1324	1310	1.1
2	1341	1318	1.7
3	1345	1327	1.4
4	1542	1576	-2.2
5	1524	1568	-2.8
Average	1415	1420	-0.3

TABLE 5. SFGT FLUE GAS FLOWRATE QA AUDIT RESULTS

Test No.	Flowmeter (scfm)	Audit - Method 2 (scfm)	Error (%)
1	987	1102	-10.4
2	986	1204	-18.1
3	978	1165	-15.3
4	1026	1186	-13.5
5	1023	1236	-17.2
6	984	1290	-23.7
7	992	1123	-11.7
8	984	1085	-9.3
9	1000	1116	-10.4
10	1000	1126	-11.2
Average	996	1163	-14.4

NH_3 Injection Rate

The results of the NH_3 injection rate QA audits at both the HZ and SFGT pilot plants are presented in Table 6. As shown, the relative error at both plants was consistent and had the same magnitude. This error was within the accuracy limits of the measurement technique (i.e., absorption followed by weight gain measurement). The results indicate that accurate (±10 percent) NH_3 injection measurements were made at both pilot plants.

TABLE 6. NH_3 INJECTION RATE AUDITS AT THE HZ AND SFGT PILOT PLANTS

Test No.	Process Measurement (gms NH_3/min)	Audit-Absorption (gms NH_3/min)	Error %
HZ Pilot Plant			
1	11.8	12.7	-7.1
2	11.9	12.5	-4.8
Average	11.85	12.6	-6.0
SFGT Pilot Plant			
1	10.4	9.7	6.9
2	9.7	9.0	7.3
3	9.8	9.1	7.8
Average	9.97	9.27	7.6

Reactor Pressure Drop

The results of the reactor pressure drop QA audits at the HZ and SFGT pilot plants are presented in Tables 7 and 8, respectively. As shown, the process measurements and audit results at both pilot plants were in excellent agreement. This indicates that the pressure drop measurements made by Chemico and UOP during the pilot plant test program were accurate.

TABLE 7. HZ REACTOR PRESSURE DROP AUDIT RESULTS

Test No.	Process Measurement (in H_2O)	Audit-Magnehelic (in H_2O)	Error (%)
1	1.05	1.0	5.0
2	1.05	1.0	5.0
3	1.04	1.0	4.0
4	1.04	1.0	4.0
5	1.04	1.0	4.0
6	1.05	1.0	5.0
Average	1.045	1.0	4.5

TABLE 8. SFGT REACTOR PRESSURE DROP AUDIT RESULTS

Test No.	Process Measurement ($in H_2O$)	Audit-Magnehelic ($in H_2O$)	Error (%)
1	10.75	10.5	2.4
2	10.75	10.5	2.4
3	10.25	11.0	-6.8
4	10.00	10.5	-4.8
5	9.75	10.0	-2.5
6	9.50	9.75	-2.6
7	10.50	10.25	2.4
Average	10.21	10.36	-1.4

Reactor Operating Temperature

The results of the reactor operating temperature QA audits at the HZ and SFGT pilot plants are presented in Tables 9 and 10 respectively. As shown, the process measurements and the audit results at both plants were in excellent agreement. This indicates that the reactor inlet temperatures measured by Chemico and UOP were accurate. Since Chemico demonstrated reactor performance over a range of temperatures, these results are not critical to the HZ process but they are to the SFGT process. UOP did not document SFGT process performance at reduced temperatures, so the process measurements define a lower limit for process operation.

TABLE 9. HZ REACTOR OPERATING TEMPERATURE AUDIT RESULTS

Test No.	Process Measurement (°F)	Audit Thermocouple (°F)	Error (%)
1	717	681	5.3
2	720	691	4.2
3	719	684	5.1
4	722	690	4.6
5	718	684	5.0
Average	719.2	686	4.8

TABLE 10. SFGT REACTOR OPERATING TEMPERATURE AUDIT RESULTS

Test No.	Process Measurement (°F)	Audit Thermocouple (°F)	Error (%)
1	772	780	-1.0
2	762	769	-0.9
3	781	794	-1.6
4	781	790	-1.1
5	785	769	2.1
6	787	801	-1.7
7	780	802	-2.7
8	776	799	-2.9
9	778	788	-1.3
Average	778	788	-1.3

DCN 80-203-001-11-14

APPENDIX B

SECONDARY EMISSIONS SAMPLING RESULTS

TECHNICAL NOTE

RESULTS OF SECONDARY EMISSION SAMPLING AT THE EPA SPONSORED NO_x PILOT PLANTS

December, 1980

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SECTION 1

INTRODUCTION

The Environmental Protection Agency sponsored pilot scale tests of two selective catalytic reduction (SCR) processes for NO_x removal. The processes tested were the Hitachi-Zosen (HZ) process and the Shell flue gas treatment (SFGT) process which also removes SO_2. The contractors responsible for design and operation of these pilot units were Chemico Air Pollution Control Corporation (HZ process) and the Process Division of UOP (SFGT process). In both cases, these contractors were responsible for collection, evaluation, and reporting of test data.

As part of the pilot scale test program, EPA contracted Radian Corporation to conduct an independent evaluation of the performance of both pilot units. This independent evaluation consisted of several steps including:

- A quality assurance program to check measurements being made by the process operators,
- A sampling program to quantify changes in secondary process emissions across the SCR reactors, and
- A program to certify the performance of the continuous NO_x monitors (and SO_2 monitors at the SFGT pilot unit) using EPA reference methods.

This technical note presents the results of the sampling program to quantify changes in secondary process emissions. Results of the quality assurance program and the certification tests are contained in separate technical notes.

SECTION 2

POLLUTANTS OF INTEREST

SCR processes have been operated commercially in Japan for several years, but there is a surprising lack of data on secondary emissions from these processes. Therefore, one objective of EPA's pilot plant test program was to quantify changes in secondary emissions across the SCR reactor. Based on available information about SCR processes and on concerns expressed by the professional community, a group of pollutants was selected for detailed sampling and analysis at the EPA sponsored pilot plants. These pollutants include:

- ammonia (NH_3),
- sulfur trioxide (SO_3),
- particulate loading and composition,
- carbon monoxide (CO),
- hydrocarbons (C_1 through C_6),
- hydrogn cyanide (HCN),
- nitrosoamines, and
- nitrous oxide (N_2O).

The following discussion briefly examines the reasons for measuring each of these pollutants, while Section 3 contains a description of the pilot units and the process streams which were sampled during the test program. Section 4 presents the results of the sampling effort, along with a brief description of the sampling and analysis procedures used.

Ammonia (NH_3)

Ammonia was measured at the reactor outlet at each pilot plant to quantify the emission rate under normal operating conditions. Ammonia is injected upstream of the catalyst in an SCR process to react with NO_x reducing it to molecular nitrogen. Under normal operating conditions, it is expected that some NH_3 will pass through the catalyst unreacted. This unreacted NH_3 represents a secondary process emission which can present significant operational and possibly environmental problems, depending on the emission rate.

Sulfur Trioxide (SO_3)

Sulfur trioxide was measured at each pilot unit to determine if any change in concentration occurs in the NO_x reduction reactor. The reason for measuring SO_3 across the reactor differs for each plant. The Hitachi-Zosen system contains a catlyst which can promote oxidation and it is possible that SO_3 may be produced in the reactor due to SO_2 oxidation. On the other hand, UOP has indicated that the SFGT system may actually reduce flue gas SO_3 concentrations due to reaction with the material used in the reactor. Measurement of the SO_3 concentration at the reactor inlet and outlet was made to quantify the magnitude of any changes which occur in the reactor at both pilot plants.

Particulate Loading and Composition

Particulate samples were collected and analyzed at the pilot units. Particulate loading was measured to document the loading the reactor is exposed to and thus demonstrate the ability of the reactor to operate under high particulate loadings. Particulate composition was measured to attempt to determine if any catalyst is being eroded from the reactor. This was done by examining particulate composition at the reactor inlet and outlet and determining if any increase in the concentration of the elements present in the catalyst occurs.

Carbon Monoxide (CO) and Hydrocarbons (HC)

Carbon monoxide and hydrocarbons were measured at the reactor inlet and outlet to determine if any change occurs in the concentration of these pollutants across the reactor. These two pollutants are of interest since they can both be oxidized by oxygen or NO_x. As a consequence, it is possible that the reactor may also reduce the emission levels of CO and/or HC.

Hydrogen Cyanide (HCN), Nitrosoamines, and Nitrous Oxide (N_2O)

Hydrogen cyanide, nitrosoamines and nitrous oxide were measured to determine if any change in the concentration of these compounds occurs in the pilot system reactors. While no concrete evidence exists to indicate that HCN, nitrosoamines, or N_2O are produced, concern has been expressed that the presence of NH_3 and the catalyst may result in production of one or more of these compounds. The sampling program was designed to measure each of these compounds and document any change in their concentrations across the reactor.

SECTION 3

PILOT PLANT DESCRIPTION

EPA has sponsored the demonstration of two SCR processes applied to coal-filled boilers. The size of these units was nominally 0.5 MWe equivalent and each was designed to remove 90 percent of the incoming NO_x. The SFGT pilot unit was also designed to achieve simultaneous removal of 90 percent of the SO_2 in the flue gas. The following discussion presents a brief description of each process in general and a specific description of the EPA sponsored pilot plants.

3.1 CHEMICO/HITACHI-ZOSEN PLANT

Chemico Air Pollution Control Corporation's pilot demonstration of the Hitachi-Zosen selective catlytic reduction (SCR) process is located at Georgia Power Company's Plant Mitchell Station in Albany, Georgia. The process has been commercially applied to numerous oil and gas-fired boilers in Japan. This pilot plant is a demonstration of the process for coal-fired applications.

The SCR process utilizes ammonig (NH_3) to selectively reduce NO_x to molecular nitrogen (N_2) in a catalytic reactor. The overall chemical reactions are shown in Equations 1 and 2.

$$4\ NO(g) + NH_3(g) + O_2(g) \rightarrow 4\ N_2(g) + 6\ H_2O(g) \qquad (1)$$

$$2\ NO_2(g) + 4\ NH_3(g) + O_2(g) \rightarrow 3\ N_2(g) + 6\ H_2O(g) \qquad (2)$$

In the process, NH_3 is injected into flue gas which is at a temperature between 300°C and 400°C. The gas then passes through a catalytic reactor where the reduction reactions (Equations 1 and 2) occur rapidly.

The HZ pilot plant processed a 1000-1500 SCFM slipstream of flue gas which was withdrawn between the economizer and the air preheater of the coal-fired unit 3 at the Plant Mitchell Station. At this point, the flue gas contained the full particulate loading from the boiler. The slipstream from the boiler was first passed up through a flue gas heater for temperature control. NH_3 was then injected into the flue gas which flowed down through the reactor. After exiting the reactor, the gas passed through a cyclone particulate collector, a fan, and it then returned to the boiler flue gas duct. The particulate collector was included in the pilot unit to minimize abrasion in the fan.

Figure 1 is a schematic of the HZ pilot plant which shows the location of the sampling ports used during the test program. The flue gas temperature was approximately 315°C at the inlet sample port and 370°C at the outlet port. Full particulate loadings were present at both sampling locations.

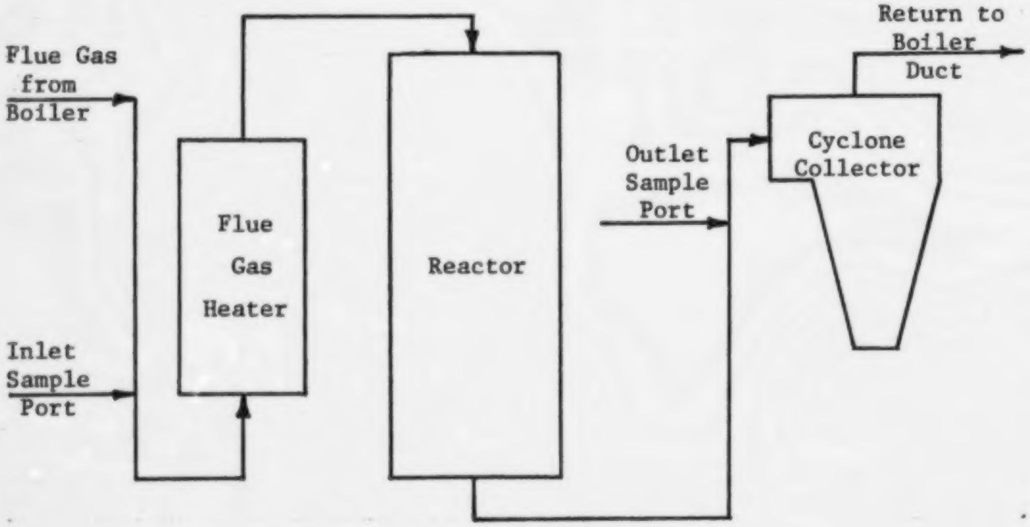

Figure 1. Schematic of the HZ pilot plant.

3.2 UOP/SFGT PILOT PLANT

The Process Division of UOP has operated a pilot demonstration of the Shell Flue Gas Treatment (SFGT) process at Tampa Electric Company's Big Bend Station in North Ruskin, Florida. The process has been commercially applied on an oil-fired boiler in Japan, while the pilot plant was a coal-fired demonstration.

This SCR process is unique in that it removes both SO_2 and NO_x . Copper supported on alumina is used as an SO_2 "acceptor". SO_2 and O_2 react with the acceptor as shown in Equation 3.

$$SO_2(g) + \tfrac{1}{2} O_2(g) + CuO(s) \rightarrow CuSO_4(s) \qquad (3)$$

Copper oxide and, to a greater extent, the copper sulfate ($CuSO_4$) produced by the SO_2 acceptance reaction, act as a catalyst for the reduction of NO_x by NH_3 according to Equations 1 and 2.

As SO_2 is removed in the reactor, the acceptor becomes "loaded" and SO_2 emissions begin to increase. Once the time averaged SO_2 removal reaches the design level (e.g., 90 percent), flue gas flow to the reactor is shut off and the $CuSO_4$/CuO are reconverted to Cu metal. In this regeneration step, a steam/hydrogen mixture is passed through the reactor and a concentrated SO_2 stream is produced. The regeneration reactions are illustrated by Equations 4 and 5.

$$CuSO_4 + H_2 \rightarrow CuO + SO_2 + H_2O \qquad (4)$$

$$CuO + H_2 \rightarrow Cu + H_2O \qquad (5)$$

The SO_2 produced by the regeneration of the reactor can be further processed to recover the sulfur as sulfuric acid or elemental sulfur.

The SFGT pilot plant processed a 1000 scfm slipstream of flue gas which was withdrawn between the economizer and the air preheater of the coal-fired unit 2 at Tampa Electric Company's Big Bend Station. Flue gas from the boiler contained full particulate loading and was heated by in-line burners before entering the reactor. Flue gas flowed up through the reactor during acceptance of SO_2 and bypassed the reactor during the regeneration of the acceptor. During the program, some tests were conducted in which the reactor was fully loaded with SO_2 and NO_x was the only pollutant removed. While these tests were conducted, the reactor processed flue gas continuously. During cyclic operation, the acceptance period ranged from 50 to 70 minutes, with an average of 65 minutes, while the regeneration period ranged from 22 to 40 minutes, with an average of 29 minutes.

Figure 2 is a schematic of the SFGT pilot plant which shows the location of the sampling ports used during the test program. Flue gas temperature was approximately 400 °C at both the inlet and outlet sampling ports. Full particulate loadings were present at both sampling locations.

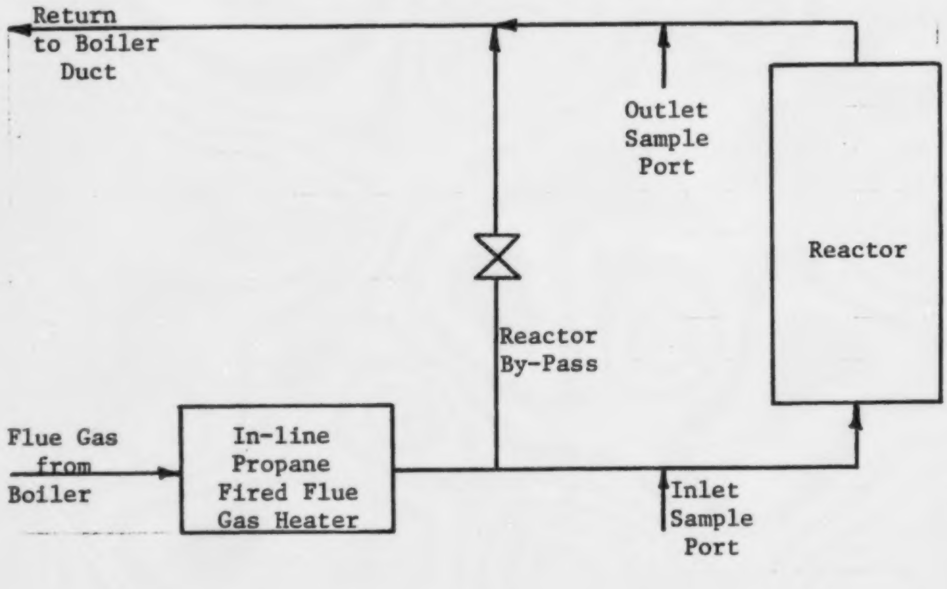
Return to Boiler Duct
Outlet Sample Port
Reactor
Reactor By-Pass
Flue Gas from Boiler
In-line Propane Fired Flue Gas Heater
Inlet Sample Port

Figure 2. Schematic of the SFGT pilot plant.

SECTION 4

RESULTS

The stack sampling program was conducted by Radian during the period June through August, 1980. A mobile laboratory was used during the program and most of the analytical work was completed on-site. The results of the stack sampling work are summarized in Tables 1 and 2 which show inlet and outlet concentrations of the species measured at the HZ and SFGT pilot plants respectively. It should be noted that no results for N_2O are presented due to the fact that the measuring technique proved unsatisfactory.

As shown in Table 1, the concentrations of CO, HC, HCN and nitrosoamines at the HZ pilot plant were all below the detection limit of the techniques used. This indicates that no significant change in the concentrations of these species occurred in the reactor. Table 1 does show significant increases in the concentrations of NH_3 and SO_3 emitted from the reactor, while the apparent change in particulate loading is believed to be the result of random error or unaccounted for stratification in the ducts.

Table 2 shows the results from the sampling program of the SFGT unit. Concentrations of HCN and nitrosoamines were below the detection limit, again showing that no significant change in the concentration of these species occurred in the reactor. Decreases in both the HC and CO concentrations were measured across the reactor. This change is probably due to oxidation of these pollutants across the reactor. It is believed that the relatively high levels of CO and HC's measured were due to emissions from the in-line propane burners located upstream of the reactor. As shown, a decrease in SO_3 concentration was also measured across the reactor. This decrease is due to removal of SO_3 from the flue gas via reaction with the acceptor. The apparent change

TABLE 1 - STACK SAMPLING RESULTS AT HZ PILOT UNIT

Flue Gas Component	Reactor Inlet Concentration[1]	Reactor Outlet Concentration[1]	Measurement Technique
Nitrosoamines[2]	<5 μg/dscm	<5 μg/dscm	Absorption, Extraction, Gas Chromatograph w/nitrogen specific detector
Hydrogen Cyanide[2]	<.01 mg/dscm	<.01 mg/dscm	Absorption, distillation, titration
Ammonia	Not measured	54.8 ppmv (dry basis)	Absorption, distillation, titration
Sulfur Trioxide	8.4 ppmv (dry basis)	20.7 ppmv (dry basis)	Controlled Condensation, Ion Chromatograph
Hydrocarbons[2] (C_1-C_6)	<1.0 ppmv	<1.0 ppmv	Gas Chromatograph Flame Ionization Detector
Carbon Monoxide[2]	<0.017%	<0.017%	Fischer Gas Partitioner
Particulate Loading	7.1 gm/dscm	7.7 gm/dscm	In stack filter

[1] Average of 3 or more tests

[2] Below the detection limit

TABLE 2 - STACK SAMPLING RESULTS AT UOP PILOT PLANT

Flue Gas Component	Reactor Inlet Concentration[1]	Reactor Outlet Concentration[1]	Measurement Technique
Nitrosoamines[4]	<5 µg/dscm	<5 µg/dscm	Absorption, Extraction, Gas Chromatograph w/nitrogen specific detector
Cyanides[4]	<.01 mg/dscm	<.01 mg/dscm	Absorption, distillation, titration
Ammonia	Not measured	15.3 ppmv (dry basis)[2] 49.0 ppmv (dry basis)[3]	Absorption, distillation, titration
Sulfur Trioxide	11.4 ppmv (dry basis)	0.1 ppmv (dry basis)	Controlled condensation, ion chromatograph
Hydrocarbons (C_1-C_6)	28.5 ppmv	21.0 ppmv	Gas Chromatograph Flame Ionization Detector
Carbon Monoxide	0.13%	<0.017%[4]	Fischer Gas Partitioner
Particulates	8.9 gm/dscm	6.3	In stack filter

[1] Average of 2 or more tests

[2] During simultaneous SO_x/NO_x removal tests

[3] During NO_x removal only tests

[4] Below the detection limit

in particulate concentration is believed to be due to unaccounted for stratification in the ducts.

The following discussion examines the stack sampling results in more detail. In addition, a brief discussion of the analytical techniques are presented.

Ammonia

Ammonia samples were collected at the reactor outlet at both the HZ and SFGT pilot plants. At the SFGT pilot plant, samples were collected during both cyclic and NO_x only operation. The samples collected during cyclic operation were taken over the course of an entire cycle yielding an average NH_3 concentration at the reactor outlet during the cycle.

Ammonia emission samples were collected by filtering the flue gas in the duct and drawing the sample through a glass-lined probe into two impingers containing 5 wt percent H_2SO_4. A composite sample was produced by combining the two impinger solutions with the washings from the sample probe. A 250 ml aliquot of the composite was taken for analysis of NH_3 nitrogen by a distillation/titration procedure. The aliquot was buffered with a sodium borate buffer solution, and the pH adjusted to 9.5 using sodium hydroxide. This mixture was then distilled for approximately one hour, until more than 200 ml of distillate was collected. The distillate was captured subsurface in a boric acid indicating solution. This product solution was then titrated with a standard .02 N sulfuric acid titrant.

The results of the NH_3 emissions sampling at the HZ pilot plant are presented in Table 3. As shown, the NH_3 emissions were quite high, averaging about 55 ppm for all the tests. This emission rate is much higher than the expected rate of 10 to 20 ppm, and it could have serious impacts on equipment located downstream of the SCR process. In addition, NH_3 emissions of 50 ppm could result in formation of an ammonium sulfite/bisalfite plume downstream

TABLE 3 - HITACHI-ZOSEN/CHEMICO PILOT PLANT NH_3 EMISSIONS

Date	Time	NO_x In (ppm wet)	NH_3:NO_x	NH_3 Emission (ppm dry)
7-18	13:45 - 14:05	459	0.91	45
7-18	15:11 - 15:31	451	0.97	46
7-29	14:54 - 15:20	466	0.92	49
7-30	10:37 - 10:57	453	0.92	60
8-1	12:23 - 12:48	469	0.99	44
8-2	11:17 - 11:42	479	0.99	63
8-2	18:50 - 19:10	440	1.05	54
8-5	15:29 - 15:57	450	0.89	58
8-6	16:53 - 17:13	460	1.01	74*
8-7	11:17 - 11:42	493	0.89	41*
8-7	13:15 - 13:40	482	0.98	68*

*Note: Sample analyzed by pH adjustment, direct nesslerization/spectrophotometry instead of pH adjustment, distillation/titration as for other samples. Tests from 7-29 and 8-1 were run with both methods with good agreement.

of a wet FGD system. The reason for the high NH_3 emission rate is unclear at this time, but is probably due to an inadequate amount of catalyst in the reactor. Other possibilities, such as a high NH_3 injection rate have been checked and do not explain the measured NH_3 emission rate.

The results of the NH_3 measurements at UOP are presented in Table 4. As shown, the samples taken during the NO_x only tests indicate an average NH_3 emission rate of 49 ppm which is quite similar to the results from the HZ NH_3 emission tests. The samples collected during the cyclic operation of the SFGT process exhibit results which are quite different from the non-cyclic operation. Samples collected during cyclic operation show an average NH_3 concentration of about 15 ppm in the gas exiting the reactor. This emission rate is more in line with expectations prior to the start of the pilot scale tests, and should not present serious problems downstream of the SCR reactor. It should be noted, however, that the measured NH_3 concentration is an average over the acceptance period and no information is available on the instantaneous NH_3 emission rate over the course of a cycle.

Currently, no explanation has been found for the marked difference in NH_3 emission rates during cyclic and non-cyclic operation at essentially the same operating conditions (i.e., flue gas flow, temperature, NH_3 injection rate). One possibility is that Cu and CuO promote NH_3 oxidation at a higher rate than $CuSO_4$ does. Another possibility is that the metal surfaces in the reactor strongly adsorb NH_3. During non-cyclic operation this adsorption would occur only once and the surfaces would quickly become saturated with NH_3. During cyclic operation NH_3 would be desorbed during regeneration. Consequently, the reactor internals would always have some capacity for adsorbing NH_3, thus lowering the NH_3 emission rate during acceptance.

TABLE 4 - SFGT PILOT PLANT NH_3 EMISSIONS

Date	Time	UOP Cycle #	NO_x In (ppm dry)	NH_3:NO_x	NH_3 Emissions (ppm dry)
6-21	16:12 - 17:12	875	380	1.17	15
6-23	12:49 - 13:52	903	420	1.21	16
6-24	13:26 - 14:36	918	390	1.31	22
6-26	13:23 - 14:20	948	375	1.25	17
6-26	17:52 - 18:48	951	No UOP Data		16
6-27	15:06 - 16:02	965	No UOP Data		11
6-28	15:49 - 16:52	982	392	1.17	12
6-28	17:27 - 18:32	983	402	1.19	13
6-30	15:27 - 17:06	1004	No UOP Data		16
7-11	14:01 - 14:23	NO_x Only	420	1.18	47
7-15	14:50 - 15:15	NO_x Only	327	1.21	52
7-15	18:28 - 18:53	NO_x Only	224	1.38	48

TABLE 5 - CHANGE IN SO_3 CONCENTRATION ACROSS THE REACTOR IN THE HZ PROCESS

Date	Time	SO_3 Inlet (ppm dry)	SO_3 Outlet (ppm dry)	SO_2 Oxidation (%)
7-23	16:30 - 17:20	11.0	25.3	1.5
7-24	16:50 - 17:40	7.5	14.8	1.1
7-25	16:25 - 17:10	6.6	21.9	1.9

TABLE 6 - CHANGE IN SO_3 CONCENTRATION ACROSS THE REACTOR IN THE SFGT PROCESS

Date	Time	SO_3 Inlet (ppm dry)	SO_3 Outlet (ppm dry)	Removal (%)
10-8	14:40 - 15:40	10.4	0.095	99.1
10-8	17:15 - 18:45	12.4	0.108	99.1

Sulfur Trioxide

Sulfur trioxide was collected using a controlled condensation system. The SO_3 was selectively condensed at 80°C in a modified Graham condenser. The sample was recovered by rinsing the condenser coil with deionized water and the sulfate concentration of the coil rinse was measured by ion chromatagraphy. The results of the SO_3 sampling are presented in Tables 5 and 6.

For the three test results from the HZ pilot plant, shown in Table 5, an average of 1.5 percent of the inlet SO_2 is oxidized to SO_3 across the reactor. This effect is to be expected since a primary component of the catalyst, vanadium pentoxide, is used commercially as a SO_2 oxidation catalyst. The increase in SO_3 concentration, by an average of 12.3 ppm, has potentially important downstream impacts. First, the resultant higher sulfuric acid (H_2SO_4) dewpoint decreases the amount of heat that a boiler air preheater can safely extract from the flue gas without suffering increased corrosion. This can be a significant energy penalty. Increased maintenance costs and decreased service life for the preheater or downstream equipment, due to H_2SO_4 attack could result. Another potential impact is an increase in ammonium bisulfate (NH_4HSO_4) formation in the preheater from the reaction of SO_3 and water with residual ammonia exiting the SCR reactor. This can result in an increased pressure drop for the system. Maintenance costs could increase due to more frequent cleaning of the preheater. Finally, any additional SO_3 that passed through the preheater would most likely result in increased H_2SO_4 emissions. Conventional flue gas desulfurization (FGD) systems are not very effective for capturing the H_2SO_4 aerosols or mist that would form.

For the two tests run at UOP's plant, an average of 99% of the SO_3 was removed from the flue gas. This SO_3 removal capability of the system is also important. By lowering the H_2SO_4 dewpoint, it may be possible to operate the air preheater at a lower flue gas exit temperature and thus recover more energy in the preheater. This can be a significant energy savings. Lower SO_3 concentrations should minimize downstream impacts, decreasing emissions and maintenance and increasing equipment life.

Particulates

Particulates were collected by filtering the flue gas in stack (EPA Reference Method 17) with a 30 by 100 mm glass fiber sampling thimble. Traverses of the duct were conducted to ensure a representative sample. The samples were collected isokinetically in accordance with established EPA methods. The samples were weighed to determine grain loadings and a composite of three samples was analyzed to determine the elemental composition of the particulates.

The results of the particulate loading measurements are presented in Tables 7 and 8. At the HZ pilot plant, the grain loading averaged 7.1 gm/dscm at the inlet and 7.7 gm/dscm at the outlet. No particulate matter is produced within the system, so the 8% difference in grain loading values is probably attributable to small random errors. It is also possible that stratification of the particulates existed in the ducts, since the sample ports were located close to downstream disturbances.

At the SFGT plant, the grain loading averaged 8.9 gm/dscm at the inlet and 6.3 gm/dscm at the outlet. No large air leaks are present in the system to dilute the flue gas, so the 29% difference in grain loading values is due to an error in sampling. The magnitude of the difference suggests a systematic error in the sampling procedure. Because of the location of sample ports on the SFGT pilot unit, it was only possible to traverse the duct in a single plane. Since the sample ports were also located close to disturbances at the SFGT plant, it is conceivable that

TABLE 7 - GRAIN LOADINGS MEASURED AT THE HZ PILOT PLANT

Date	Time	Inlet (gm/dscm)	Outlet (gm/dscm)
7-29	17:50 - 18:50	7.5	7.8
7-30	17:02 - 18:02	6.9	8.4
7-31	14:09 - 15:09	6.9	-
7-31	18:08 - 19:08	-	6.9

TABLE 8 - GRAIN LOADINGS MEASURED AT SFGT PILOT PLANT

Date	Time	Inlet (gm/dscf)	Outlet (gm/dscf)
6-19	10:47 - 11:27	8.3	6.7
6-19	13:55 - 14:35	11.2	6.8
6-19	17:05 - 17:45	7.4	5.5

representative sampling of the duct was not possible using this single plane.

Table 9 presents the results of the elemental analysis of the particulates collected at the HZ pilot plant. This analysis was conducted to determine if catalyst erosion was causing an increase in the concentration of Vandium (V) or Titanium (Ti) in the particulates leaving the reactor. As shown in Table 9, an apparent increase in all elements occurs across the reactor, but the relative concentrations on V and Ti remain constant. This indicates that there is no measurable change in the concentration of V or Ti in the particulates exiting the reactor. The apparent change could be due to several factors. One possibility is the presence of an inert material (e.g., unburned carbon) in the inlet sample. This material may have entered the sample due to contamination, or if it is indeed unburned carbon, it may have been burned in the flue gas heater located between the reactor inlet and outlet sample ports. In any event, it can be concluded that no significant increase in the concentrations of V or Ti in the particulates occurred due to catalyst erosion.

Table 10 presents the results of the elemental analysis of the particulates collected at the SFGT pilot plant. At this plant, the elements of interest are Alumina (Al) and Copper (Cu). As shown, no significant change in the composition of the particulates was measured with respect to these elements. The changes which are shown in Table 10 are probably due to random errors in the sampling on analysis technique and are not representative of real changes in particulate composition. Therefore, it can be concluded that no significant increase in the concentrations of Al or Cu in the particulates occurred due to catalyst erosion.

Carbon Monoxide and Hydrocarbons

Samples were collected by cooling a filtered flue gas stream to about 200°F and then passing it through a Perma-Pure dryer to remove moisture. Samples were collected in Mylar gas bags that had been purged several times with the conditioned gas.

TABLE 9 - RESULTS OF PARTICULATE ANALYSIS AT THE HZ PILOT PLANT

Component[1]	In	Out	Out/In
Al	10.7%	13.0%	1.21
Ca	8200 ppm	9900 ppm	1.21
Fe	4.9%	6.0%	1.22
K	2.0%	2.5%	1.25
Mg	6300 ppm	7800 ppm	1.24
Mn	190 ppm	240 ppm	1.26
Sn	490 ppm	680 ppm	1.40
Na	4200 ppm	4700 ppm	1.12
Si	18%	23%	1.28
Zn	190 ppm	250 ppm	1.32
Cu	150 ppm	170 ppm	1.13
Ti	5800 ppm	6900 ppm	1.19
V	270 ppm	330 ppm	1.22

[1] Concentrations are on a mass fraction basis

TABLE 10 - RESULTS OF PARTICULATE ANALYSIS AT THE SFGT PILOT PLANT

Component[1]	In	Out	Out/In
Al	8.6%	8.0%	.93
Ca	1.8%	1.8%	1.00
Fe	12%	11.1%	0.93
K	1.5%	1.4%	0.93
Mg	5100 ppm	5000 ppm	0.98
Mn	300 ppm	320 ppm	1.07
Sn	270 ppm	270 ppm	1.00
Na	4300 ppm	5100 ppm	1.19
Si	20%	16%	0.80
Zn	410 ppm	720 ppm	1.76
Cu	96 ppm	100 ppm	1.04
Ti	5400 ppm	5100 ppm	0.94
V	255 ppm	340 ppm	1.33

[1] Concentrations are on a mass fraction basis

The samples were analyzed on-site using a Fisher Gas Partioner Model 1200 TCD-GC and an AID portable Gas Chromatograph. The gas samples were introduced into the instruments, and the retention times and peak heights were compared to those obtained from mixes of standard gases. At the HZ pilot plant the GC became inoperative and C_1-C_6 hydrocarbon samples were collected in snout* bags and transported to Radian's Austin Laboratories where they were analyzed within a week of collection on a Tracor Model 560 FID-CG. The results are presented in Tables 11 and 12.

As shown in Table 11, the concentration of both CO and HC's at the HZ pilot plant were below the detection limit of the analysis techniques so no conclusion could be drawn concerning the impact of the catalyst on these pollutants. However, at the SFGT pilot plant, decreases in the concentrations of both CO and HC were measured across the reactor. This decrease is attributed to oxidation of the CO and HC's by the catalyst forming CO_2 and H_2O. The oxidation of these compounds was not unexpected since the NO_x reduction reaction is actually an oxidation of NH_3 by NO_x and the catalyst is basically an oxidation catalyst. It should be noted that the high levels of CO and HC's at the SFGT pilot plant were probably a result of incomplete combustion in the propane burners used for flue gas temperature control upstream of the reactor.

Hydrogen Cyanide (HCN)

Cyanide samples were collected by bubbling filtered flue gas through a 10% sodium hydroxide solution. Samples were shipped to Radian's Austin Laboratories for analysis. It was originally proposed to measure the concentration of cyanide spectrophotometrically with a pyridine-barbituric

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*Consists of layers of polyester, polyvinyl chloride, aluminum, polyamide and polyethylene.

TABLE 11 - FISHER GAS PARTIONER AND G.C. DATA FROM THE HZ PILOT PLANT

Sampling Location	Species (as % of total flue gas)				
	CO_2	O_2	N_2	CO	C_1-C_6
Inlet	17.8	4.4	69.7	<0.017	<1 ppm
Outlet	17.2	4.9	68.5	<0.017	<1 ppm

TABLE 12 - FISHER GAS PARTIONER AND G.C. DATA FROM THE SFGT PILOT PLANT

Sampling Location	Species (as % of total flue gas)				
	CO_2	O_2	N_2	CO	CH_4
Inlet	17.5	4.8	70.5	0.13	28.4 ppm
Outlet	17.6	4.8	70.3	<0.017	21.0 ppm

The total C_1-C_6 hydrocarbon concentration was the same as the CH_4 concentration.

acid reagent, but this method proved to be unfeasible due to inferference from SO_2 absorbed in the sodium hydroxide solution. A silver nitrate ($AgNO_3$) titration method was used instead. The silver ions complex with the cyanide to form $Ag(CN^-)_2$. The excess Ag^+ is detected by paradimethylaminobenzalrhodanine, which undergoes a yellow to salmon color change in the presence of Ag^+ ions.

The $AgNO_3$ titrametic method employed by Radian could detect cyanide at a level equal to or greater than 0.01 mg/dscm. The concentration of cyanide at Chemico and UOP pilot plants was below this limit of detection at both the inlet and outlet sampling ports. This indicates that no significant increase in the flue gas HCN concentration occurs across the reactor at either pilot plant.

Nitrosoamines

Nitrosoamine samples were collected by bubbling filtered flue gas through a 1N potassium hydroxide solution. The samples were packed in ice and shipped to Radian's Austin laboratories. There each sample was serially extracted with distilled-in-glass methylene chloride to remove the organic species from the sample matrix. The methylene chloride extracts were then combined and concentrated by evaporation to less than 10 ml. Hexane (10 ml) was added and each extract was reconcentrated to remove the methylene chloride. The resulting hexane extracts were then analyzed by GC.

The samples were initially analyzed by a nitrogen specific detector. The chromatogrphic data was generated using a 6' x 4mm 10 percent carbowax 20M + two percent KOH column. Two separate injections were conducted for each sample. The first injection at 110°C isothermal was employed for low molecular weight nitrosoamines such as N-nitrosodimethylamine. A second injection at 220°C isothermal was employed for higher boiling species such as N-nitrosodiphenylamine. Several small peaks were observed; none of these matched the retention time of known nitrosoamines in the standard used. The samples were then analyzed by a Hall electroconductivity detector operated in the nitrosoamine specific mode using a 8' x 2 mm 15 percent LAC-2R-446 Column at 145° isothermal. No peaks were observed in these analyses.

The GC/MS analysis could detect nitrosoamines at a level equal to or greater than 5 ug/dscm. The concentration of nitrosoamines at the Chemico and UOP pilot plants was below this limit of detection at both the inlet and outlet sampling ports. This shows that no significant change in nitrosoamine concentrations occurred across the reactor at either pilot plant.

Nitrous Oxide (N_2O)

Grab samples of flue gas were collected in Mylar bags. The gas was cooled and filtered to remove condensed ammonium salts and water vapor. The samples were then injected into a Miran 1A Gas Analyzer (Wilks Scientific Corporation) and the concentration of N_2O was determined by infra red (IR) spectral analysis.

Nitrous oxide is not normally measured in flue gas studies and there is no generally accepted procedure. The method used in the sampling program was not sensitive enough to detect the presence of N_2O. Several interfering peaks combined with the low level of any N_2O present made determination of the N_2O concentration impossible.

In order to measure N_2O, it would have been necessary to concentrate it prior to analysis. One technique which has been used for measuring low N_2O levels is cryogenic trapping and gas chromatography. A silica gel column is used to concentrate the N_2O in the gas sample. After withdrawal from the duct, particulates, water, and CO_2 are successively removed from the sample. The gas is then passed through a gel-concentration column maintained at -70°C which further concentrates the N_2O. The N_2O is desorbed by flushing with helium. The gas sample passes through a separation column and the N_2O

concentration is measured with a thermal conductivity detector.

This method is routinely used to measure atmospheric level of N_2O (250-300 ppb), but can detect levels down to at least 50 ppb.

SUMMARY

The stack sampling program conducted by Radian was designed to quantify changes in the emission rate of secondary pollutants from the SCR process. The results of this program showed that:

- A significant quantity of NH_3 is emitted from the HZ process and from the SFGT process during non-cyclic (NO_x only) operation,
- The HZ process produces SO_3 by oxidation of SO_2 at a rate equivalent to 1 to 2 percent of the SO_2 in the flue gas.
- The SFGT process removes nearly all the SO_3 in the flue gas entering the reactor. This could have a beneficial impact on downstream equipment which may be subject to acid corrosion.
- The particulate loadings in the processed flue gas at both pilot plants was about 7 gm/dscm which is typical of many coal-fired applications.
- No significant change in particulate composition was measured across the reactor at either pilot unit.
- The concentrations of both CO and HC's were reduced across the SFGT reactor. It is believed this reduction was due to oxidation. No change was measured in the concentration of CO or HC's at the HZ pilot unit due to the fact the concentrations were below the detection limit of the analytical techniques.
- No significant change in the concentrations of HCN or nitrosoamines occurred at either pilot unit.
- The technique used for measuring N_2O proved unsatisfactory for the quantity of N_2O (if any) present in the flue gas at either pilot unit.

APPENDIX C

CONTINUOUS MONITOR CERTIFICATION TEST RESULTS

TECHNICAL NOTE

RESULTS OF THE CONTINUOUS MONITOR CERTIFICATION TESTS AT THE EPA SPONSORED NO_x PILOT PLANTS

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SECTION 1

INTRODUCTION

The Environmental Protection Agency sponsored pilot scale tests of two selective catalytic reduction (SCR) processes for NO_x removal. The processes tested were the Hitachi-Zosen (HZ) process and the Shell flue gas treatment (SFGT) process which also removes SO_2. The contractors responsible for design and operation of these pilot units were Chemico Air Pollution Control Corporation (HZ process) and the Process Division of UOP (SFGT process). In both cases, these contractors were responsible for collection, evaluation, and reporting of test data.

As part of the pilot scale test program, EPA contracted Radian Corporation to conduct an independent evaluation of the performance of both pilot units. This independent evaluation consisted of several steps including:

- A quality assurance program to check measurements being made by the process operators,
- A sampling program to quantify changes in secondary process emissions across the SCR reactors, and
- A program to certify the performance of the continuous NO_x monitors (and SO_2 monitors at the SFGT pilot unit) using EPA reference methods.

This technical note presents the results of certification tests to assure the accuracy of the data collected by the continuous NO_x and SO_2 monitors. Results of the secondary emissions sampling program and the quality assurance program are contained in separate technical notes.

SECTION 2

OBJECTIVE AND APPROACH

The objective of the continuous monitor certification tests was to insure the accuracy of the data generated by the continuous monitors at the two pilot plants. In conjunction with the quality assurance program, the certification tests were expected to provide accurate characterization of the pilot plant's performance permitting the data collected by Chemico and UOP to be used as a basis for a more detailed process evaluation.

The approach used in conducting the continuous monitor certification tests was based on a formal procedure which has been developed by EPA to insure the accuracy of monitors measuring emissions from sources which must comply with new source performance standard emission limitations. According to the procedure developed by EPA, a continuous emission monitor must pass a number of performance tests in order to be certified. These tests include:

- calibration error,
- response time,
- 2- and 24-hour zero drift,
- 2- and 24-hour calibration drift, and
- relative accuracy.

The performance specifications for each of the above certification tests are shown in Table 1. These specifications are those contained in the Federal Register, Vol. 44, No. 197, Wednesday, October 10, 1979 - "Proposed Rules: Standards of Performance for New Stationary Sources; Continuous Monitoring Performance Specifications".

TABLE 1. CONTINUOUS MONITORING SYSTEM PERFORMANCE AND EQUIPMENT SPECIFICATIONS

Certification Test	Performance Specification
Calibration Error	≤ 5 percent for mid-range and high level calibration values
Response Time	≤ 15 minutes
Zero Drift (2-hour)	≤ 2 percent of Span[1] value
Zero Drift (24-hour)	≤ 2.5 percent of Span[1] value
Calibration Drift (2-hour)	≤ 2 percent of Span[1] value
Calibration Drift (24-hour)	≤ 2.5 percent of Span[1] value
Relative Accuracy	≤ 20 percent of reference test data in terms of emission standard[2] or 10 percent of the applicable standard, whichever is greater

[1] Span refers to the range of the emission monitor (e.g., 0-500 ppm).
[2] Emission standards are expressed in terms of pollutant mass emissions per unit of heat input.

Because the pilot plants were operated as experimental systems, the operating characteristics of the continuous monitors were different than those of a continuous monitor system for a typical commercial scale application. In particular, the pilot plant continuous monitors received considerably more operator attention in an effort to insure the quality of the data being collected. As a consequence, not all the continuous monitor performance specifications were strictly adhered to. The major emphasis of the certification tests conducted at the pilot plants was to insure the relative accuracy of the continuous monitors. The other certification tests were considered of secondary importance.

The following discussion presents the procedure for conducting each certification test, identifies areas where the certification tests at the pilot plants differed from those outlined in the performance specifications, and presents reasons for the differences. The certification results are presented in detail in Section 3. For more details of the certification test procedures, the reader is referred to the Federal Register mentioned above.

Calibration Error

Calibration error is a measure of the ability of a continuous monitor to accurately analyze the concentration of a calibration gas. To determine calibration error, a series of 15 measurements are made; 5 each of high and mid-level calibration gas concentrations and 5 of zero gas (air). The measurements are made such that the same gas concentration is not measured two or more times in a row (i.e., non-consecutively). The calibration error is then determined by the difference between the concentration of the calibration gas (which has been verified by one of several techniques defined in the CEM performance specifications) and the continuous monitor readings. Specifically the error is defined by Equation 1.

$$\text{Calibration Error} = \frac{|\bar{X}| + |CI_{95}|}{RV} \qquad (1)$$

where $|\bar{X}|$ = absolute value of the mean difference between the monitor reading and the calibration gas concentration.

RV = concentration of the calibration gas.

$|CI_{95}|$ = absolute value of the 95 percent confidence interval which is defined by Equation 2.

$$CI_{95} = \frac{t_{.975}}{n(n-1)^{\frac{1}{2}}} \left(n \sum X_i^2 - \left(\sum X_i \right)^2 \right)^{\frac{1}{2}} \qquad (2)$$

where n = the number of measurements (in this case 5)

t = 2.776 (for 5 measurements)

X_i = difference between the continuous monitor reading and the calibration gas concentration for individual readings.

For the continuous monitor to pass the calibration error test, the error as defined by Equation 1 must be less than or equal to 5 percent for both the mid- and high-range calibration gases. There was no deviation from this procedure in conducting the calibration error test at either pilot plant.

Response Time

Response time is a measure of the time which elapses before a continuous monitor responds to a change in the pollutant concentration in a duct. To determine response time, zero gas is introduced into the continuous monitor's sampling system at the duct/sample line interface. Once the monitor reading stabilizes at zero, the sampling system is switched from zero gas to monitoring the stack effluent and the time required for the monitor to reach a stable reading is determined. This is the upscale response time. Subsequently, the downscale response time is determined by introducing high-level calibration gas into the continuous monitor sampling system at the duct/sample line interface. Once the monitor's reading stabilizes at the high level gas concentration, stack gas is introduced into the sample line and the time required for the monitor's reading to reach a stable value downscale is determined. This procedure is repeated three times and the mean upscale and downscale response times are determined. The maximum of these values must be less than 15 minutes for the continuous monitor to pass this test.

This method of measuring response time represents a slight change from previous EPA performance specifications which were the ones followed during the certification tests at the pilot plants. In the previous certification procedures, response time was determined by alternately introducing zero and high-level calibration gas into the sample line at the duct/sample line interface. Upscale response time was that required to stabilize the CEM system reading after the switch from air to high-level calibration gas while downscale response time was measured in the opposite manner. This measure of response time should provide an accurate indication of system response provided care is taken to prevent excessive span gas pressure in the sample line.

Zero and Calibration Drift

Zero and calibration drift are measures of how the continuous monitor's response to zero and calibration gases change with time. To measure two-hour drift, zero and high level calibration gases are introduced into the instrument at two-hour intervals. The differences between the monitor readings and the zero or calibration gas concentrations are recorded and a total of 15 sets of data are collected. Drift is then calculated using Equations 1 and 2 where the reference value (RV) equals the range of the continuous monitor and $t_{.975}=2.145$ (for 15 tests). 24-hour drift is measured in a similar manner. At the start of a 24-hour period the monitor is calibrated and zeroed and then no further adjustments are made. After 24 hours, zero and calibration drift are recorded and the instrument is recalibrated. A total of 7 measurements are required to determine 24-hour drift and Equations 1 and 2 are used. For 7 measurements, $t_{.975}=2.447$.

Because the pilot plants were operated as experimental units, the accuracy of continuous monitors was of particular concern. As a consequence, the calibration and zero settings on the continuous monitors were adjusted about once per hour for the SFGT pilot plant (generally at the start and completion of an acceptance period), and every two hours at the HZ pilot plant. Obviously, the 24-hour drift test is not meaningful under these circumstances and, in the case of the SFGT pilot plant, the two-hour drift test could not be completed strictly according to performance specifications. Instead, the zero and calibration drift was determined for the period between initial and final calibration and zeroing of a monitor.

Relative Accuracy

Relative accuracy is the most important test in determining the performance of the continuous monitors. This test is comparison of the continuous monitor's analysis of stack gas with a stack gas analysis as determined by EPA reference methods (Method 3 for O_2 and CO_2, Method 6 for SO_2, and Method 7 for NO_x). Relative accuracy is determined by making a minimum of 9 reference method tests (for Method 7, one test requires three samples) and comparing the results to the continuous monitor readings during the time the reference tests were collected. In addition, for determining the relative accuracy of NO_x and SO_2 continuous monitors, simultaneous reference method tests for O_2 are required so the NO_x and SO_2 concentrations can be converted to a mass emissions per unit of heat input (e.g., lb/10^6 Btu) basis.

After the reference method tests are completed and the continuous monitor and reference method test results are converted from concentrations to a mass emission per unit heat input basis, the relative accuracy can be determined. Relative accuracy is calculated using Equations 1 and 2 where the reference value (RV) is equal to the mean of the reference method tests and $t_{.975}$=2.306 (for 9 tests).

This procedure was followed exactly at the HZ pilot plant. And 9 sets of reference method tests for both SO_2 and NO_x were completed at the inlet and outlet of the SFGT pilot plant reactor. However, reference method tests for O_2 or CO_2 were not included because UOP did not operate a diluent monitor. As a result, the CEM data could not be converted to a mass emission per unit of heat input basis. In the case of the SFGT pilot plant this does not impact the validity of the relative accuracy tests because: (1) the reactor operated under 7.5 kPa (30 in H_2O) pressure so no dilution occurred between the reactor inlet and outlet, and (2) the measurements made by the continuous monitors were intended to demonstrate the ability of the process to achieve a specific percentage reduction in NO_x and SO_2 emissions based on pollutant concentrations rather than a reduction in emissions below a specific mass emission rate per unit heat input.

SECTION 3

CONTINUOUS MONITOR CERTIFICATION TEST RESULTS

The certification tests conducted at the HZ and SFGT pilot plants were discussed in Section 2 of this technical note. This section presents a summary and individual results from the certification tests. It also includes the results of reference method tests on the calibration gases used during the certification test program.

Summary

Table 2 summarizes the results of the continuous monitor certification tests for both the HZ and SFGT pilot plants. As shown, the test results for all the continuous monitors met the performance specifications with one exception; the relative accuracy of the outlet NO_x monitor at the SFGT pilot plant was over 50 percent while the performance specifications require a relative accuracy of 20 percent or less. These data indicate that, with the exception of the SFGT outlet NO_x analyzer, the continuous monitors were making accurate measurements of flue gas NO_x and SO_2 concentrations. It should be noted that 24-hour zero and calibration tests were not included in the certification tests since the instruments were calibrated at least every two hours, thus making the 24-hour drift tests meaningless. In addition, at the SFGT plant, only one SO_2 monitor was used, so the values for all tests except response time and relative accuracy are identical.

The poor relative accuracy of the outlet NO_x analyzer shown in Table 2 would tend to indicate that the monitor was making inaccurate measurements of flue gas NO_x concentrations. However, there are several factors which must be considered when evaluating these test results. First, the absolute error in

TABLE 2. CONTINUOUS MONITOR CERTIFICATION TEST RESULTS

Certification Test	Performance Specification	SFGT Pilot Plant				HZ Pilot Plant	
		Inlet SO_2[1] Monitor	Outlet SO_2[1] Monitor	Inlet NO_x Monitor	Outlet NO_x Monitor	Inlet NO_x Monitor	Outlet NO_x Monitor
Calibration error							
-high level	≤5%	1.4	1.4	3.85	2.52	1.40	4.70
-mid level	≤5%	0.7	0.7	4.62	2.62	4.39	2.68
Response time	≤15 min	0.8	1.3	1.7	0.8	1.4	1.6
Zero drift (2-hour)	≤2%	0.25	0.25	0.64	1.04	1.20	0.05
Calibration drift (2-hour)	≤2%	0.49	0.49	1.35	1.18	1.93	1.78
Relative accuracy	≤20%[2]	14.0	8.6	12.6	52.3	14.1	10.5

[1] One instrument was used to measure both inlet and outlet of the reactor.

[2] Alternatively, ≤10 percent of the applicable emissions standard.

the Method 7 versus the monitor measurements was only 16 ppm on the average. This is a relatively small difference considering the accuracy of the Method 7. procedures. At low NO_x levels, similar to those encountered at the reactor outlet, EPA found the Method 7 analysis to be accurate to only ± 35 percent. A second factor, which indicates that the outlet NO_x monitors performance was within acceptable limits, is that the performance specifications require the relative accuracy be less than or equal to 20 percent or 10 percent of the applicable standard, whichever is greater. Use of the standard as a basis for relative accuracy calculations is in recognition of the inaccuracy of the Method 7 analysis at low levels. For example, using the NSPS for bituminous coal fired sources as a basis, the relative accuracy of the outlet NO_x monitor is approximately 5 percent, which is within acceptable limits. Because the relative accuracy of the outlet NO_x monitor was within 10 percent of the applicable standard and because of the documented poor performance of Method 7 at low NO_x concentrations, it was determined that the outlet NO_x monitor was performing acceptably.

Overall, the results of the certification tests indicate that the continuous NO_x and SO_2 monitors at both pilot units were performing acceptably. Therefore, the data collected during the pilot plant tests by Chemico and UOP are representative of the pilot plant's performance. This is especially true in light of the extensive monitor maintenance program carried out by both Chemico and UOP which was designed to insure the accuracy and quality of the performance data collected.

The preceding discussion presented a summary of the monitor certification test results. Details of individual measurement results follow. This includes the results of reference method analysis of calibration gases.

Calibration Gases

The calibration gases used during the certification tests were analyzed prior to the tests to insure the manufacturer's reported concentrations were accurate. The results of these analyses are presented in Table 3. As shown, the reference method test results were within 5 percent of the manufacturer's reported concentrations except for the mid-range SO_2 calibration gas. In this case, the SO_2 concentration was assumed to be that determined by the reference method results while the other gas concentrations were assumed equal to the manufacturer's reported concentration.

TABLE 3. COMPARISON OF MANUFACTURER'S REPORTED CALIBRATION GAS CONCENTRATIONS WITH REFERENCE METHOD TEST RESULTS

Calibration Gas		Reference Method Test Result (ppm)				Error[2]
Description	Concentration[1] ppm	1	2	3	Average	(%)
High-Range SO_2	2690	2631	2844	2792	2756	-2.4
Mid-Range SO_2	1470	1612	1618	1613	1614	-8.9
Inlet						
High-Range NO_x	930	914	914	911	913	+1.9
Mid-Range NO_x	515	464	557	525	515	0
Outlet						
High-Range NO_x	91.9	87.2	88.2	95.0	90.1	+2.0
Mid-Range NO_x	50.4	54.2	51.9	43.5	49.9	+1.1

[1] This is the manufacturer's reported concentration.
[2] Error = (manufacturer's reported concentration - reference method result) ÷ (reference method result)

Calibration Error

The calibration error measurements for the HZ pilot plant are presented in Table 4 while the SFGT pilot plant measurements are presented in Table 5. As shown, only one set of data was taken for the SO_2 monitor at the SFGT pilot plant since this instrument was used to measure both inlet and outlet concentrations. The work-up of the HZ pilot data is presented in Tables 6-9 while the work-up of the SFGT pilot plant data is presented in Tables 10-15. As shown, all the monitors passed the calibration error tests.

TABLE 4. RAW DATA: CALIBRATION ERROR TESTS AT THE HZ PILOT PLANT

	Inlet NO_x Monitor[1]		Outlet NO_x Monitor	
Run No.	Calibration Gas Concentration (ppm)	Measurement System Reading (ppm)	Calibration Gas Concentration (ppm)	Measurement System Reading (ppm)
1	955	948	0	0.4
2	0	2	91.9	87.2
3	955	947	50.4	49.3
4	515	533	91.9	89.5
5	0	4	0	0.3
6	515	532	50.4	49.2
7	955	948	0	0.3
8	0	6	91.9	89.8
9	955	941	50.4	49.3
10	515	538	0	0.4
11	0	5	50.4	49.3
12	515	536	91.9	89.0
13	0	6	50.4	49.9
14	955	955	91.9	91.0
15	515	534	0	0.4

[1] This monitor failed the initial test and was later retested with a different high-range calibration gas.

TABLE 5. RAW DATA: CALIBRATION ERROR TESTS AT THE SFGT PILOT PLANT

	Inlet NO_x Monitor		Outlet NO_x Monitor		SO_2 Monitor	
Run No.	Calibration Gas Concentration (ppm)	Measurement System Reading (ppm)	Calibration Gas Concentration (ppm)	Measurement System Reading (ppm)	Calibration Gas Concentration (ppm)	Measurement System Reading (ppm)
1	930	905	0	1	0	0
2	0	14	515	505	2690	2740
3	930	902	930	916	1614	1620
4	515	495	515	504	2690	2688
5	0	9	930	908	0	-4
6	515	494	0	1	1614	1604
7	930	922	930	907	0	-8
8	0	11	515	501	1614	1616
9	930	922	0	1	2690	2664
10	515	520	515	504	0	0
11	0	10	0	1	2690	2676
12	515	529	930	916	1614	1616
13	0	5	515	507	2690	2680
14	515	532	930	919	0	-4
15	930	958	0	1	1614	1604

TABLE 6. HZ NO_x INLET MONITOR: HIGH-RANGE CALIBRATION ERROR RESULTS

Run No.	Calibration Gas Concentration (ppm)	Measurement System Reading (ppm)	Difference (ppm)
1	955	948	-7
3	955	947	-8
7	955	948	-7
9	955	941	-14
14	955	955	0
ΣX_i =			-36
$\lvert\bar{X}\rvert$ =			7.2
$\lvert CI_{95}\rvert$ =			6.17
Relative Accuracy =			1.4%

TABLE 7. HZ NO_x INLET MONITOR: MID-RANGE CALIBRATION ERROR RESULTS

Run No.	Calibration Gas Concentration (ppm)	Measurement System Reading (ppm)	Difference (ppm)
4	515	533	18
6	515	532	17
10	515	538	23
12	515	536	21
15	515	534	19
ΣX_i =			98
$\lvert\bar{X}\rvert$ =			19.6
$\lvert CI_{95}\rvert$ =			2.99
Relative Accuracy =			4.39%

TABLE 8. HZ NO_x OUTLET MONITOR: HIGH-RANGE CALIBRATION ERROR RESULTS

Run No.	Calibration Gas Concentration (ppm)	Measurement System Reading (ppm)	Difference (ppm)
2	91.9	87.2	-4.7
4	91.9	89.5	-2.4
8	91.9	89.8	-2.1
12	91.9	89.0	-2.9
14	91.9	91.0	-0.9
ΣX_i =			-13
$\lvert\bar{X}\rvert$ =			2.6
$\lvert CI_{95}\rvert$ =			1.72
Relative Accuracy =			4.70%

TABLE 9. HZ NO_x OUTLET MONITOR: MID-RANGE CALIBRATION ERROR RESULTS

Run No.	Calibration Gas Concentration (ppm)	Measurement System Reading (ppm)	Difference (ppm)
3	50.4	49.3	-1.1
6	50.4	49.2	-1.2
9	50.4	49.3	-1.1
11	50.4	49.3	-1.1
13	50.4	49.9	-0.5
ΣX_i =			-5
$\lvert\bar{X}\rvert$ =			1
$\lvert CI_{95}\rvert$ =			0.35
Relative Accuracy =			2.68%

TABLE 10. SFGT NO_x INLET MONITOR: HIGH-RANGE CALIBRATION ERROR RESULTS

Run No.	Calibration Gas Concentration (ppm)	Measurement System Reading (ppm)	Difference (ppm)
1	930	905	-25
3	930	902	-28
7	930	922	-8
9	930	922	-8
15	930	958	+28
ΣX_i =			-41
$\|\bar{X}\|$ =			8.2
$\|CI_{95}\|$ =			27.65
Relative Accuracy =			3.85%

TABLE 11. SFGT NO_x INLET MONITOR: MID-RANGE CALIBRATION ERROR RESULTS

Run No.	Calibration Gas Concentration (ppm)	Measurement System Reading (ppm)	Difference (ppm)
4	515	495	-20
6	515	494	-21
10	515	520	5
12	515	529	14
14	515	532	17
ΣX_i =			-5
$\|\bar{X}\|$ =			1
$\|CI_{95}\|$ =			22.77
Relative Accuracy =			4.62%

TABLE 12. SFGT NO_x OUTLET MONITOR: HIGH-RANGE CALIBRATION ERROR RESULTS

Run No.	Calibration Gas Concentration (ppm)	Measurement System Reading (ppm)	Difference (ppm)
3	930	916	-14
5	930	908	-22
7	930	907	-23
12	930	916	-14
14	930	919	-11
ΣX_i =			-84
$\lvert\bar{X}\rvert$ =			16.8
$\lvert CI_{95}\rvert$ =			6.65
Relative Accuracy =			2.52%

TABLE 13. SFGT NO_x OUTLET MONITOR: MID-RANGE CALIBRATION ERROR RESULTS

Run No.	Calibration Gas Concentration (ppm)	Measurement System Reading (ppm)	Difference (ppm)
2	515	505	-10
4	515	504	-11
8	515	501	-14
10	515	504	-11
13	515	507	-8
ΣX_i =			-54
$\lvert\bar{X}\rvert$ =			10.8
$\lvert CI_{95}\rvert$ =			2.69
Relative Accuracy =			2.62%

TABLE 14. SFGT SO_2 MONITOR HIGH-RANGE CALIBRATION ERROR RESULTS

Run No.	Calibration Gas Concentration (ppm)	Measurement System Reading (ppm)	Difference (ppm)
2	2690	2740	50
4	2690	2688	-2
9	2690	2664	-26
11	2690	2676	-14
13	2690	2680	-10
ΣX_i =			-2
$\lvert\bar{X}\rvert$ =			0.4
$\lvert CI_{95}\rvert$ =			36.59
Relative Accuracy =			1.38%

TABLE 15. SFGT SO_2 MONITOR MID-RANGE CALIBRATION ERROR RESULTS

Run No.	Calibration Gas Concentration (ppm)	Measurement System Reading (ppm)	Difference (ppm)
3	1614	1620	6
6	1614	1604	-10
8	1614	1616	2
12	1614	1616	2
15	1614	1604	-10
ΣX_i =			-10
$\lvert\bar{X}\rvert$ =			2
$\lvert CI_{95}\rvert$ =			9.29
Relative Accuracy =			0.70 %

Response Time

Table 16 presents the results of the response time measurements at the HZ and SFGT pilot plants. As shown all the continuous monitors had response times much lower than the 15 minute limit required by the performance specifications. The relatively rapid response times recorded are due, in part, to the short sample lines (less than 25 meters) at the pilot plants. These results indicate that even though the response time measurements were made in accordance with previous certification procedures (and not the current proposed procedures) the response times of the pilot plant continuous monitors are acceptable.

TABLE 16. RESPONSE TIME DATA FROM THE HZ AND SFGT PILOT PLANTS

	Response Time (min)[1]					
	HZ Monitors		SFGT Monitors			
Test No.	NO_x In	NO_x Out	NO_x In	NO_x Out	SO_2 In	SO_2 Out
1	1.3	1.8	1.5	0.7	0.7	1.3
2	1.4	1.5	3.2	0.8	0.8	1.6
3	1.5	1.6	0.4	0.8	0.8	1.0
Ave.	1.4	1.6	1.7	0.8	0.8	1.3

[1] Response time was defined as the time it took the instrument to register 95 percent of a step change in concentration of gas to the monitor.

Zero and Calibration Drift

As discussed earlier, the pilot plants were operated as experimental units. As a result, the accuracy of the continuous monitors was of critical importance and they were calibrated quite frequently (as often as once an hour). By the strict definition, both the 2- and 24-hour drift tests were not applicable to the pilot plants' continuous monitors. Instead, zero and calibration drift data were collected for the monitors prior to the routine calibration carried out by Chemico and UOP. This gives an indication of the drift experienced by the monitors between routine calibrations and is approximately equivalent to the 2-hour drift tests.

TABLE 17. HZ PILOT PLANT ZERO AND CALIBRATION DRIFT TEST RESULTS

Run No.	Inlet NO_x Monitor[1]		Outlet NO_x Monitor[2]	
	ΔZero (ppm)	ΔCal (ppm)	ΔZero (ppm)	ΔCal (ppm)
1	-12	-12	0	2.7
2	40	7	0	-5.0
3	8	-15	0	-3.0
4	-20	23	-0.1	2.5
5	0	40	0	3.5
6	7	-10	0.1	3.6
7	-4	13	0	-3.0
8	-10	10	0	0
9	-35	15	0	4.0
10	-1	9	0	-4.0
11	-3	40	-0.1	2.0
12	-15	-30	-0.1	-2.0
13	-17	-42	0	0
14	18	39	0	2.0
15	45	-25	-0.1	-2.0
X_i	1	72	-0.3	1.3
$\lvert\bar{x}\rvert$	0.07	4.8	0.02	0.09
$\lvert CI_{95}\rvert$	11.91	14.45	0.03	1.69
Error (%)	1.20	1.93	0.05	1.78

[1] The range of this monitor was 0-1000 ppm.

[2] The range of this monitor was 0-100 ppm.

TABLE 18. SFGT PILOT PLANT ZERO AND CALIBRATION DRIFT TEST RESULTS

Run No.	Inlet NO_x Monitor ΔZero (% of Span)	ΔCal (% of Span)	Outlet NO_x Monitor[1] ΔZero (ppm)	ΔCal (ppm)	SO_2 Monitor ΔZero (% of Span)	ΔCal (% of Span)
1	1.0	-0.5	-0.7	-4.3	-0.3	-0.9
2	-0.5	0.3	-4.7	-2.3	0.3	-0.5
3	0.4	1.0	-4.7	-3.0	0.2	-0.5
4	-0.3	1.5	1.0	-2.7	0.4	-0.5
5	0.1	1.0	0	-3.0	0.3	-0.3
6	-0.5	-1.3	0.7	-2.3	0.2	-0.3
7	-0.2	-1.8	-2.0	2.0	0.3	-0.4
8	-0.1	-0.1	-2.0	1.3	0.4	-0.4
9	-0.5	-2.0	-4.3	10.0	0.2	-0.7
10	-0.5	-3.5	1.0	3.7	-0.2	1.0
11	-0.5	1.1	1.3	1.7	-0.4	0.3
12	-1.0	0.4	2.0	-10.0	0	0.1
13	-1.1	-2.5	4.0	1.0	0.3	1.0
14	-0.4	2.0	-3.3	-1.7	0	-0.3
15	-1.0	-2.0	-4.3	3.0	-0.4	-0.3
ΣX_i	-5.1	-6.4	-16	-6.6	-1.3	-2.7
$\lvert\bar{X}\rvert$	0.34	0.43	1.07	0.44	0.09	0.18
$\lvert CI_{95}\rvert$	0.30	0.92	1.54	2.51	0.16	0.31
Error (%)	0.64	1.35	1.04	1.18	0.25	0.49

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[1] The range of this monitor was 0-250 ppm.

Relative Accuracy

Relative accuracy is the most important of the certification tests conducted since this compares the continuous monitor results to reference method analyses of the flue gas. In addition, the relative accuracy tests provide an independent check of the pilot plants' performance while the other certification tests only yield performance information about the instruments.

Tables 19, 20, and 21 present the raw data and results for the HZ relative accuracy tests while Tables 22 and 23 present this information for the SFGT pilot plant. As shown, all monitors except the NC_x outlet at the SFGT pilot plant meet the performance specifications. The fact that the SFGT outlet NO_x analyzer does not meet the relative accuracy specification is not significant in terms of the performance data collected. The average NO_x reduction recorded by the instruments during the relative accuracy tests was 84.9 percent, while the Method 7 results indicate an average NO_x reduction of 87.4 percent.

TABLE 19. HZ NO_x INLET MONITOR: RELATIVE ACCURACY TEST DATA

	Monitor Readings		Reference Method Results		
Test No.	NO_x (ppm wet)	O_2 (% wet)	NO_x (ppm dry)	O_2 (% wet)	Moisture (%)
1	485	3.4	469	3.0	7.8
2	443	3.6	442	3.0	7.0
3	479	3.4	430	2.5	8.0
4	469	3.3	443	2.5	7.9
5	489	3.8	439	3.0	7.5
6	460	3.5	453	3.0	8.4
7	435	2.8	442	2.0	8.1
8	447	2.9	469	2.5	7.9
9	484	3.6	524	3.0	8.5

TABLE 20. HZ NO_x OUTLET MONITOR: RELATIVE ACCURACY TEST DATA

Test No.	Monitor Readings NO_x (ppm wet)	Monitor Readings O_2 (% wet)	Reference Method Results NO_x (ppm dry)	Reference Method Results O_2 (% wet)	Reference Method Results Moisture (%)
1	73.7	3.4	73.2	3.5	8.1
2	66.6	3.6	62.8	3.3	7.4
3	57.3	3.4	52.4	2.7	8.2
4	57.8	3.4	56.4	2.5	8.1
5	63.9	3.2	55.0	2.5	7.8
6	64.0	3.9	70.1	4.0	8.7
7	79.4	2.9	81.4	2.0	8.4
8	82.5	2.5	87.9	2.0	8.1
9	78.8	3.3	87.5	3.5	8.8

TABLE 21. HZ NO_x MONITORS: RELATIVE ACCURACY TEST RESULTS

Test No.	Inlet Monitor Monitor ($lb/10^6Btu$)	Inlet Monitor Method 7 ($lb/10^6Btu$)	Inlet Monitor Difference ($lb/10^6Btu$)	Outlet Monitor Monitor ($lb/10^6Btu$)	Outlet Monitor Method 7 ($lb/10^6Btu$)	Outlet Monitor Difference ($lb/10^6Btu$)
1	0.711	0.657	0.054	0.105	0.106	-0.001
2	0.657	0.605	0.052	0.097	0.088	0.009
3	0.687	0.576	0.111	0.082	0.071	0.011
4	0.668	0.590	0.078	0.082	0.075	0.007
5	0.717	0.601	0.116	0.091	0.073	0.018
6	0.663	0.621	0.042	0.094	0.102	-0.008
7	0.603	0.572	0.031	0.111	0.105	0.006
8	0.623	0.624	-0.001	0.112	0.114	-0.002
9	0.702	0.718	-0.016	0.112	0.123	-0.011
ΣX_i	-	-	0.467	-	-	0.029
$\lvert\bar{X}\rvert$	-	0.618	0.052	-	0.095	0.003
$\lvert CI_{95}\rvert$	-	-	0.035	-	-	0.007
Relative Accuracy (%)	-	-	14.1	-	-	10.5

TABLE 22. SFGT NO_x MONITORS: RELATIVE ACCURACY TEST DATA AND RESULTS[1]

Test No.	Inlet Monitor Monitor (ppm)	Inlet Monitor Method 7 (ppm)	Inlet Monitor Difference (ppm)	Outlet Monitor Monitor (ppm)	Outlet Monitor Method 7 (ppm)	Outlet Monitor Difference (ppm)
1	433	395	38	68.7	79.4	-10.7
2	408	394	14	94.7	79.2	15.5
3	438	391	47	71.9	50.6	21.3
4	395	334	61	70.0	38.6	31.4
5	398	345	53	48.0	35.1	12.9
6	427	425	2	42.3	40.7	1.6
7	387	357	30	48.3	34.8	13.5
8	313	299	14	65.0	34.5	30.5
9	357	351	6	28.3	20.6	7.7
ΣX_i	-	-	265	-	-	123.7
$\lvert\bar{X}\rvert$	-	366	29.44	-	45.9	13.7
$\lvert CI_{95}\rvert$	-	-	16.56	-	-	10.29
Relative Accuracy (%)	-	-	12.6	-	-	52.3

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[1] All concentrations are expressed on a wet basis.

TABLE 23. SFGT SO_2 MONITOR: RELATIVE ACCURACY TEST DATA AND RESULTS[1]

Test No.	Inlet Monitor			Outlet Monitor		
	Monitor (ppm)	Method 7 (ppm)	Difference (ppm)	Monitor (ppm)	Method 7 (ppm)	Difference (ppm)
1	2412	2207	205	202	192	10
2	2336	2162	174	198	189	9
3	2408	2145	263	210	205	5
4	2440	2765	175	206	203	3
5	2436	2103	333	144	148	-4
6	2360	2120	240	120	119	1
7	2460	2223	237	186	224	-38
8	2472	2278	194	182	164	18
9	2444	2048	396	158	141	17
ΣX_i	-	-	2217	-	-	21
$\lvert\bar{X}\rvert$	-	2172	246.3	-	176.1	2.3
$\lvert CI_{95}\rvert$	-	-	57.7	-	-	12.9
Relative Accuracy (%)	-	-	14.0	-	-	8.6

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[1] All concentrations expressed on a wet basis.

It should be noted that the results of the SFGT relative accuracy tests are expressed as ppm instead of mass emissions of unit heat input to the boiler. This was due to the fact that there was no diluent monitor used at the SFGT pilot plant. While these results do not strictly conform to the performance specifications, they are still valid in terms of establishing process performance. This is due to the fact that the SFGT pilot plant reactor operated under positive pressure and thus no dilution occurred across the reactor. Thus the measured removals represent actual removals and not apparent changes in concentration due to dilution.

APPENDIX D

ECONOMIC PREMISES AND EQUIPMENT COSTS USED FOR COST ESTIMATE

SECTION 1

INTRODUCTION

This appendix presents the economic premises developed by TVA and used as a basis for the cost estimate prepared as part of this evaluation. It also includes the estimated equipment costs which were used to determine the total capital investment.

SECTION 2

ESTIMATED EQUIPMENT COSTS

Table 1 presents the modified estimated equipment costs for the SFGT process and compares those costs with the original TVA estimates. The modified equipment cost estimates were developed based on the ratio of material flowrates or energy requirements and standard exponential factors which relate equipment cost ratios to equipment size ratios. For all equipment except the SFGT reactor, the exponents were taken from the article: "Capital Cost Estimating" by K.M. Guthrie, Chemical Engineering, March 24, 1969. For the SFGT reactor, the costs were determined based on estimates supplied by UOP and the assumption that no economy of scale is realized for the acceptor.

As shown in Table 1, most of the equipment items are projected to increase slightly in cost with the exception of the reactor. Reactor costs are estimated to increase 44 percent, primarily due to the increased acceptor requirements. As discussed in the main report, this translates into significant increase in total capital investment and annual revenue requirements for the process.

TABLE 1. MODIFIED EQUIPMENT COST ESTIMATES

Item	Quantity	Description	Total Equipment Cost 1979$	
			TVA	Radian
Area 1 - NH_3 Storage and Injection				
1	2	NH_3 Unloading Compressor	50,000	50,000
2	11	NH_3 Storage Tanks	230,100	316,400
3	2	NH_3 Vaporizer	36,800	44,700
4	2	NH_3 Air Mixture Blower	13,500	16,400
Sub-Total Area 1			$330,400	$427,500
Area 2 - Flue Gas Fans				
1	2	Flue Gas Blower	1,510,300	1,469,000
Sub-Total Area 2			$1,510,300	$1,469,000
Area 3 -				
1	8	Reactors, Internals, Catalyst	16,969,000	24,448,000
2	1	Steam Superheater	267,500	315,200
Sub-Total Area 3			$17,236,500	$24,763,200
Area 4 - Flow Smoothing				
1	1	Waste Heat Boiler	29,800	41,900
2	1	Steam Drum	38,100	52,200
3	1	Steam Blowdown Drum	13,700	18,800
4	1	Main Quench Tower	189,600	212,300
5	4	Quench Water Circulating Pumps	110,700	121,200
6	1	Quench Feed Filter	30,000	29,900
7	1	Quench Water Cooler	793,100	918,100
8	1	Steam Stripper	51,100	57,100
9	2	Stripper Bottoms Pump	16,000	17,400
10	1	Stripper Bottoms Filter	15,000	16,400

Continued/

TABLE 1. (Continued)

Item	Quantity	Description	Total Equipment Cost 1979$	
			TVA	Radian
Area 4 - Flow Smoothing (Continued)				
11	1	Stripper Bottoms Cooler	50,000	56,700
12	1	Compressor Suction Drum	41,800	39,600
13	1	SO_2-Rich Gas Compressor	100,000	93,500
14	1	Compressed Gas Quench Tower	68,100	64,500
15	1	Gas Holding Drum	127,000	120,300
Sub-Total Area 4			$1,674,000	$1,859,900
Area 5 - Steam Naphtha Reformer				
1	1	Packaged Steam Naphtha Reformer	3,220,000	3,684,800
Sub-Total Area 5			$3,220,000	$3,684,800
Area 6 - Sulfuric Acid Plant				
1	1	Contact Sulfuric Acid Plant	5,719,000	5,719,000
Sub-Total Area 6			$5,719,000	$5,719,000
TOTAL, Areas 1-6			$29,692,200	$37,923,400

SECTION 3

ECONOMIC PREMISES

This section presents the economic premises developed by TVA and used as a basis for the cost estimates prepared as part of this study.

Capital Investment

Capital investment estimates were based on a midwestern plant location and represent projects beginning in mid-1977 and ending in mid-1980, with an average cost basis for scaling of mid-1979. Direct investments were calculated using the average annual *Chemical Engineering* cost indices for the period up to 1975 and the recent TVA projections for the period 1976-1981 shown in Table 2. Actual equipment cost estimates are based on 1978 cost information obtained from engineering-contracting, processing, and equipment companies.

Costs related to equipment, material, and construction-labor shortages with accompanying overtime pay incentive and costs for the generation facilities for electricity used by the NO_x removal processes and FGD unit were not included.

TABLE 2. COST INDICES AND PROJECTIONS

Year	1970	1971	1972	1973	1974	1975	1976[a]	1977[a]	1978[a]	1979[a]	1980[a]	1981[a]
Plant	125.7	132.3	137.2	144.1	165.4	182.4	197.9	214.7	232.9	251.5	271.6	293.3
Material[b]	123.8	130.4	135.4	141.9	171.2	194.7	210.3	227.1	245.3	264.9	286.1	309.0
Labor[c]	137.4	146.2	152.2	157.9	163.3	168.6	183.8	200.3	218.3	237.9	259.3	282.6

[a] Projections.

[b] Same as index in *Chemical Engineering* for "equipment, machinery, supports."

[c] Same as index in *Chemical Engineering* for "construction labor."

Direct Investment--

The purchase cost of the process equipment and the cost of materials and labor for the installation of this equipment were included. Also, the cost of piping and insulation, ductwork, excavation, site preparation, foundation, structural, roads and railroads, electrical, instrumentation, buildings, painting, services, and pond construction required for each unit area were estimated. The costs for the SFGT process was estimated based on the flow diagram and equipment lists.

Services, utilities, and miscellaneous costs were estimated at 6% of the total direct investment. This expense covers allocated costs for the use of such power plant facilities as maintenance shops, stores, communications, security, and offices. Parking lots, walkways, landscaping, fencing, and vehicles are also included in the service facility estimate.

Indirect Investment--

The indirect investment includes costs for engineering design and supervision, architect and engineering contractor expenses, construction expenses, contractor fees, and contingency. The engineering design and supervision and contingency factors are based on proven design, not first-of-a-kind installation.

Engineering design and supervision--This indirect investment factor was estimated using a technique that correlates the number of major pieces of process equipment with drafting room man-hour and engineering design costs.

Architect and engineering (A&E) contractor expenses--This cost was based directly upon the engineering design and supervision costs. A&E expense was assumed to be 25% of the portion of engineering design and supervision costs associated with major equipment.

Construction expense--Construction expense was estimated as a function of the direct investment using the following equation.

$$\text{Construction expense} = 0.25\ (x)^{0.83}$$

where x = direct investment in $\$ \times 10^{-6}$

Construction facilities (which include costs for mobile equipment, temporary lighting, construction roads, raw water supply, safety and sanitary facilities, and other similar expenses incurred during construction) are considered a part of construction expenses.

Contractor fees--The relationship between contractor fees and total direct investment used to estimate the cost of contractor fees was:

$$\text{Contractor fees} = 0.096\ (a)^{0.76}$$

where a = direct investment in $\$ \times 10^{-6}$

Contingency--The contingency was assumed to be 20% of the sum of total direct investment, engineering design and supervision costs, A&E expenses, construction expenses, and contractor fees.

Other Capital Charges--

The sum of the total direct and total indirect investment is total fixed investment. Other capital charges which must be added to this total fixed investment to obtain the total capital investment are: (1) allowance for startup and modification, (2) interest during construction, (3) land, and (4) working capital.

Allowance for startup and modifications--This expense was estimated to be 10% of the total fixed investment.

Interest during construction--This item was estimated to be 12% of the total fixed investment. This percentage is calculated as the simple interest which would be accumulated at a 10%/yr rate assuming a debt-equity ratio of 60:40 on the incremental capital investment and a 3-year project expenditure schedule as shown in Table 3.

Land--The cost of land was estimated at $3500/acre.

Working capital--Working capital consists of: (1) money invested in raw materials, supplies, and finished products carried in stock and semifinished products in the process of being manufactured; (2) accounts receivable; (3) cash retained for payment of operating expenses, such as salaries, wages, and raw material purchases; (4) accounts payable; and (5) taxes payable. For these premises, working capital was defined as the equivalent cost of 3 weeks of raw material costs, 7 weeks of direct costs, and 7 weeks of overhead costs. The raw material and direct costs do not include the costs of acceptor replacement.

TABLE 3. PROJECT EXPENDITURE SCHEDULE

Year	1	2	3	Total
Fraction of total expenditure as borrowed funds	0.15	0.30	0.15	0.60
Simple interest at 10%/yr as % of total expenditure				
Year 1 debt	1.5	1.5	1.5	4.5
Year 2 debt	-	3.0	3.0	6.0
Year 3 debt	-	-	1.5	1.5
Accumulated interest as % of total expenditure	1.5	4.5	6.0	12.0

Revenue Requirements

Annual revenue requirement calculations are based on 7000 hours of operation per year using mid-1980 operating costs and an average capital charge. Process operation schedules are assumed to be the same as the power plant operating profiles.

Direct Costs--

Direct operating costs include raw material, labor, utility and maintenance costs. The 1980 projected unit costs for the raw materials were for delivered costs to a midwestern location.

Projected 1980 utility costs are shown in Table 4. Unit costs for electricity and steam generated by the power plant are based on actual production cost including labor, fuel, depreciation, taxes, and rate base return on investment. The electricity rates are based on purchase from an independent source with full capital recovery provided and are adjusted for the quantity used. Process water rates vary with the quantity of water required. \$2/10^6 Btu was used as the cost basis for the heat credit.

Maintenance costs were estimated as a percentage of the direct investment, excluding pond construction. The maintenance factor depends on operating characteristics of the process and was estimated based on either actual operating experience or maintenance needs in similar process areas. The estimated maintenance factor for the SFGT process is 4 percent of direct investment.

TABLE 4. PROJECTED 1980 UNIT COST FOR UTILITIES

Utility	Cost, \$
Steam	2.00/MBtu
Electricity	0.029/kWh
Process water	0.06/kgal
Naphtha	0.50/gal

Indirect Costs--

Indirect costs include capital charges, projected to 1980, and overheads. Following power industry practice, regulated company economics were used for calculating the capital charges. A breakdown of the capital charges is given in Table 5. The depreciation rate is straight line based on the life of the power plant.

TABLE 5. ANNUAL CAPITAL CHARGES FOR POWER INDUSTRY FINANCING

	Percentage of total depreciable capital investment
Years Remaining Life	30
Depreciation-straight line (based on years remaining life of power unit)	3.3
Interim replacements (equipment having less than 30-year life)	0.7
Insurance and property taxes	2.0
Total rate applied to original investment	6.0
	Percentage of unrecovered capital investment[a]
Cost of capital (capital structure assumed to be 60% debt and 40% equity)	
Bonds at 10% interest	6.0
Equity[b] at 14% return to stockholder	5.6
Income taxes (Federal and State)[c]	5.6
Total rate applied to depreciation base	17.2[d]

[a] Original investment yet to be recovered or "written off".

[b] Contains retained earnings and dividends.

[c] Since income taxes are approximately 50% of gross return, the amount of taxes is the same as the return on equity.

[d] Applied on an average basis, the total annual percentage of original fixed investment for new (30 year) plants would be 6.0% + 1/2 (17.2%) = 14.6%.

Capital Charges--In estimating the regulated capital charges associated with FGT, the conventional method of considering the overall life of the power plant was used. The Federal Power Commission (FPC) recognizes the conclusion of the National Power Survey that a 30-year service life is reasonable for steam-electric plants. Because some life spans are less than 30 years, however, FPC has designated interim replacements as an allowance factor to be used in estimating annual revenue requirements. Use of this allowance following FPC-recommended practice provides for financing the cost of replacing such short-lived units. An average allowance of about 0.35% of the total investment is normally provided. However, to provide for the unknown life span of SO_2-NO_x control facilities, a larger allowance factor of 0.70% is used for new units. An insurance allowance of 0.5% is also included in the capital charges based on FPC practice. Property taxes are estimated at 1.5% of the total depreciable capital investment.

Debt-equity ratio is another component of capital charges for which variations of ratios may be expected. FPC data indicate that the long-term debt for privately owned electric utilities varied only slightly from 51.5 to 54.8% of total capitalization during the period 1965-1973. However, recent economic trends have changed the incremental debt-equity ratio because utilities are more dependent on bonds and bank loans for project funding. For these economic premises the capital structure was assumed to be 60% debt and 40% equity. The interest rate for bonds was assumed to be 10% and the return to stockholders on equity 14%. Costs of capital and income tax charges were applied to the uncovered portion of capital investment. Income taxes and return on equity are each about 50% of gross return. Since return on equity is 5.6% of total capital investment, income taxes are also 5.6% of total capital investment (see Table 24). Since most regulatory commissions base the annual permissible return on investment on the remaining depreciation base (that portion of the original investment yet to be recovered or "written off"), a portion of the annual capital charge included in the lifetime operating costs declines uniformly over the life of the power plant.

Overheads--Plant, administrative, and marketing overheads vary from company to company. Based on the various methods used in industry and illustrated in a variety of cost estimating sources, the following method of estimating overheads was used. Plant overhead was estimated as 50% of the subtotal conversion costs less utilities, which include the projected costs for labor, maintenance, and analyses. Administrative overhead was estimated as 10% of operating labor and supervision. Marketing the byproduct is also a consideration. Marketing was estimated as 10% of sales revenue.

Spent Catalyst Disposal--

For the SFGT process, the cost of disposing of the spent catalyst was added to the annual revenue requirement. For estimating purposes, the disposal cost for the catalyst carrier (alumina) was used as the basis for the yearly disposal charge.

Byproduct Sales--

In the evaluation of annual and lifetime economics, credit from sale of byproducts was deducted from the yearly operating cost to give the net effect of the SFGT process on the cost of power. A 1980 projected sales price for the byproduct sulfuric acid from the SFGT process was estimated at $30/ton.